PB87-141081

# Case Studies and Model Testing of the Metals Exposure Analysis Modeling System (MEXAMS)

Anderson-Nichols and Co., Inc., Palo Alto, CA

Prepared for

Environmental Research Lab., Athens, GA

Dec 86

U.S. Department of Commerce
National Technical Information Service
NTIS

PB87-141081

EPA/600/3-86/045
December 1986

# CASE STUDIES AND MODEL TESTING OF THE METALS EXPOSURE ANALYSIS MODELING SYSTEM (MEXAMS)

by

Allen J. Medine* and Brian R. Bicknell**

*Ecosystem Research Institute
Logan, Utah 84321
**AQUA TERRA Consultants
Mountain View, CA 94043
for
Anderson-Nichols & Co., Inc.
Palo Alto, CA 94303

Contract No. 68-03-3116

Project Officer
Lee A. Mulkey
Technical Project Monitor
Robert B. Ambrose
Assessment Branch
Environmental Research Laboratory
Athens, Georgia 30613

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL
INFORMATION SERVICE
SPRINGFIELD, VA. 22161

ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
ATHENS, GEORGIA 30613

## TECHNICAL REPORT DATA

*(Please read Instructions on the reverse before completing)*

| | | |
|---|---|---|
| 1. REPORT NO.<br>EPA/600/3-86/045 | 2. | 3. RECIPIENT'S ACCESSION NO.<br>PB87 141081/AS |
| 4. TITLE AND SUBTITLE<br>CASE STUDIES AND MODEL TESTING OF THE METALS EXPOSURE ANALYSIS MODELING SYSTEM (MEXAMS) | | 5. REPORT DATE<br>December 1986 |
| | | 6. PERFORMING ORGANIZATION CODE |
| 7. AUTHOR(S)<br>Allen J. Medine and Brian R. Bicknell | | 8. PERFORMING ORGANIZATION REPORT NO. |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS<br>Anderson-Nichols & Co., Inc.<br>Palo Alto, CA 94303 | | 10. PROGRAM ELEMENT NO.<br>ANBW1E |
| | | 11. CONTRACT/GRANT NO. |
| 12. SPONSORING AGENCY NAME AND ADDRESS<br>Environmental Research Laboratory - Athens, GA<br>Office of Research and Development<br>U.S. Environmental Protection Agency<br>Athens, GA 30613 | | 13. TYPE OF REPORT AND PERIOD COVERED |
| | | 14. SPONSORING AGENCY CODE<br>EPA/600/01 |

15. SUPPLEMENTARY NOTES

16. ABSTRACT

In the EPA's wasteload allocation/total maximum daily load program, the Agency must establish more stringent effluent limitations and guidelines for toxic chemicals (including metals) if previous limitations are not adequate to attain or maintain acceptable water quality levels. The Metals Exposure Analysis Modeling System (MEXAMS) was recently developed to assist in this effort. This model, linking a complex speciation model with an aquatic transport/fate model, should help discriminate between the fraction of metal that is dissolved and in bioavailable form and the traction that is complexed and rendered relatively notnoxic.

The MEXAMS model has been tested with data from three rivers to determine its ability to simulate fate, transport, and speciation of heavy metals in river systems. The rivers selected for study were the Naugatuck River in Connecticut and the Ten Mile River in Massachusetts, both of which receive electroplating and metal finishing wastes, and the White River in Utah, which receives metal loadings from natural sources. This report documents the tests as case studies to guide future users in the application of the model. In addition, the program has been enhanced by addition of sediment settling/resuspension to the aquatic transport submodel EXAMS.

17. KEY WORDS AND DOCUMENT ANALYSIS

| a. DESCRIPTORS | b. IDENTIFIERS/OPEN ENDED TERMS | c. COSATI Field/Group |
|---|---|---|
| | | |

| | | |
|---|---|---|
| 18. DISTRIBUTION STATEMENT<br>RELEASE TO PUBLIC | 19. SECURITY CLASS *(This Report)*<br>UNCLASSIFIED | 21. NO. OF PAGES<br>201 |
| | 20. SECURITY CLASS *(This page)*<br>UNCLASSIFIED | 22. PRICE |

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

# DISCLAIMER

The information in this report has been funded wholly or in part by the United States Environmental Protection Agency. It has been subject to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use by the U.S. Environmental Protection Agency.

# FOREWORD

As environmental controls become more costly to implement and the penalties of judgment errors become more severe, environmental quality management requires more efficient analytical tools based on greater knowledge of the environmental phenomena to be managed. As part of this Laboratory's research on the occurrence, movement, transformation, impact, and control of environmental contaminants, the Assessment Branch develops management or engineering tools to help pollution control officials achieve water quality goals.

A focus of increasing environmental concern by water quality managers is the direct toxicity of heavy metals to aquatic life and the indirect toxicity of these materials to humans and other higher organisms. To provide information on the movement of these pollutants, simulation models such as the Metals Exposure Analysis Modeling System (MEXAMS) have been developed. This report presents three case studies to test the capabilities of MEXAMS in simulating fate, transport, and speciation of heavy metals in river systems.

Rosemarie C. Russo
Director
Environmental Research Laboratory
Athens, Georgia

# ABSTRACT

In the EPA's wasteload allocation/total maximum daily load program, the Agency must establish more stringent effluent limitations and guidelines for toxic chemicals (including metals) if previous limitations are not adequate to attain or maintain acceptable water quality levels. The Metals Exposure Analysis Modeling System (MEXAMS) was recently developed to assist in this effort. This model, linking a complex speciation model with an aquatic transport/fate model, should help discriminate between the fraction of metal that is dissolved and in bioavailable form and the fraction that is complexed and rendered relatively nontoxic.

The MEXAMS model has been tested with data from three rivers to determine its ability to simulate fate, transport, and speciation of heavy metals in river systems. The rivers selected for study were the Naugatuck River in Connecticut and the Ten Mile River in Massachusetts, both of which receive electroplating and metal finishing wastes, and the White River in Utah, which receives metal loadings from natural sources. This report documents the tests as case studies to guide future users in application of the model. In addition, the program has been enhanced by addition of sediment settling/resuspension to the aquatic transport submodel EXAMS.

This report was submitted in partial fulfillment of Contract No. 68-03-3116 by Anderson-Nichols & Co., Inc., under the sponsorship of the U.S. Environmenta- Protection Agency. This report covers a period from January 1985 to September 1985, and work was completed as of September 1985.

## CONTENTS

Page

Notice.......................................... ii
Foreword........................................ iii
Abstract........................................ iv
Figures......................................... vii
Tables.......................................... ix
Acknowledgments................................. xii

1.0 Introduction................................ 1
    1.1 General................................. 1
    1.2 Modeling Pollutant Fate and Transport.......... 2

2.0 Model Descriptions.......................... 4
    2.1 EXAMS General Description............... 4
    2.2 MINTEQ General Description.............. 7
    2.3 MEXAMS General Description.............. 9

3.0 MEXAMS Input and User Guidance.............. 13
    3.1 EXAMS Input............................. 13
    3.2 MINTEQ Input............................ 17

4.0 Naugatuck River Case Study.................. 28
    4.1 Background Information.................. 28
    4.2 Input Description (MINTEQ).............. 28
    4.3 Input Description (EXAMS)............... 33
    4.4 Output (MINTEQ)......................... 40
    4.5 Output (EXAMS).......................... 46
    4.6 Output (MISP)........................... 60
    4.7 System Computational Representation and Calibration.......................... 60
    4.8 Model Results........................... 72
    4.9 Effect of Future Loadings............... 75
    4.10 Conclusions............................ 75

5.0 White River Case Study...................... 84
    5.1 White River Description................. 84
    5.2 River Segment Selected for Study........ 86
    5.3 General Water Chemistry Data Development....... 89
    5.4 Adsorption Data Development............. 93
    5.5 MINTEQ Determination of Metal Ion Activity..... 102
    5.6 Activity Kd Modeling with MINTEQ........ 110
    5.7 Activity Langmuir Modeling with MINTEQ......... 121
    5.8 Conclusion.............................. 133

6.0 Ten Mile River Case Study........................... 134
6.1 Background Information and Basin Description... 134
6.2 Ten Mile River Data............................ 137
6.3 Application of MEXAMS.......................... 149

7.0 Sediment Settling and Resuspension in MEXAMS........ 173
7.1 Overview....................................... 173
7.2 Allowed Settling Interconnections.............. 174
7.3 Settling/Resuspension Computations............. 174
7.4 Input and Output............................... 176

8.0 Recommendations..................................... 178
8.1 Enhancements................................... 178
8.2 Documentation.................................. 180
8.3 Code Integration............................... 182
8.4 Model Usage.................................... 183

REFERENCES.............................................. 184

# FIGURES

Page

2.1 Compartmentalization Examples........................ 6

2.2 MEXAMS Flowchart.................................... 10

4.1 Initial Naugatuck River Compartmentalization ....... 35

4.2 Naugatuck River Study Location...................... 38

4.3 Calibration Configurations.......................... 66

4.4 Effect of Ground water Routing on Sediment Residence Times............................................... 67

4.5 Effect of Ground water Routing on Sediment Concentration in Benthic Compartments............... 69

4.6 Dispersion Coefficients vs. Concentration of Copper in Benthic Compartments............................ 70

4.7 Kd vs. Adsorbed Concentration in the Benthic Compartments........................................ 71

4.8 Effect of Advective Flow from Compartment 6 to Compartment 5.................................... 73

4.9 Final Calibration Configuration..................... 74

4.10 Model Calibration Results for the Initial Six Compartment Configuration........................... 76

4.11 Model Calibration Results for the Final Ten Compartment Configuration........................... 78

4.12 Model Comparison to Incremental Flow Model.......... 81

4.13 The Effects of a Simulated Increased Metal Loading to Compartment 1 on the Metal Calculations............. 82

5.1 White River Study Location.......................... 88

5.2 White River Streamflow.............................. 90

5.3 Major Cation: TDS Relationships 91

5.4 Major Anion: TDS Relationships 92

5.5 Summary of Copper Adsorption Data Showing a Comparison of Pure Solid Data to White River Data 95

5.6 Zinc Adsorption Kinetics, pH = 7.50 99

5.7 Copper Adsorption Kinetics, pH = 8.20 100

5.8 Zn Ion Activity vs. Particulate Zn, pH = 8.4 111

5.9 Actual Dissolved Zinc vs. MINTEQ Prediction 122

5.10 Actual Particulate Zn vs. MINTEQ Prediction 123

5.11 Zn Ion Activity vs. Particulate Zn, pH = 7.5 124

5.12 Zn Ion Activity vs. Particulate Zn, pH = 6.7 125

5.13 Log Kd's vs. pH for Zn, Ni, and Pb 126

5.14 General Langmuir Adsorption Plot 127

5.15 CuS vs. {Cu}, pH = 7.5 129

5.16 Linear Langmuir Plot of Data 130

5.17 Langmuir Constants ($K_LS_T$) and the Activity Kd Values as a Function of pH in the White River 132

6.1 Ten Mile River Basin 135

6.2 Ten Mile River Monitoring Stations 142

6.3 Ten Mile River Point Source Discharge Locations 143

6.4 Ten Mile River Basin Reach Boundaries 156

6.5 Ten Mile River Compartment Configuration 158

8.1 Effect of Complexing Organic Upon Adsorption in Compartment 1 179

8.2 Total Metal Concentration in Water Column Compartments Under Hypothetical Natural Loading 181

# TABLES

Page

3.1 EXAMS Input Parameters describing Ecosystem Compartments and External Loadings................ 14

3.2 EXAMS Input Parameters Describing Compartment Interconnections.................................. 15

3.3 Example MINTEQ Input to Compute Activity Kd....... 20

3.4 Example MINTEQ Input to Simulate Activity Kd Adsorption........................................ 21

3.5 Example MINTEQ Input to Simulate Activity KL Adsorption........................................ 23

3.6 Surface Reactions for the Triple-Layer Model on Amorphous Iron Oxyhydroxide.................... 26

3.7 MINTEQ Input to Simulate Triple-Layer Surface Complexation...................................... 27

4.1 MINTEQ Components................................. 30

4.2 MINTEQ Input...................................... 31

4.3 Water Quality Data................................ 32

4.4 Compartment Kd Data.............................. 34

4.5 EXAMS Input....................................... 37

4.6 MISP Input........................................ 41

4.7 MINTEQ Output..................................... 42

4.8 MINTEQ Output..................................... 44

4.9 MINTEQ Output..................................... 45

4.10 MINTEQ Output.................................... 47

4.11 EXAMS Output..................................... 48

4.12 EXAMS Output.................................... 54

4.13 EXAMS Output.................................... 61

4.14 MISP Output..................................... 64

4.15 Model Results for Configuration 3................. 77

4.16 MEXAMS - Naugatuck River Model Results............ 79

4.17 Comparative Kd Data.............................. 80

5.1 The Concentration of Selected Water Quality Parameters for Several Surface Water Sources to the Study Section of the White River............... 85

5.2 Major Pollutants in Oil Shale Leachates............ 87

5.3 Water Quality Standards, Utah/Colorado............ 87

5.4 Detailed White River Water Quality................ 94

5.5 MINTEQ Input File - Aqueous Zinc Speciation........ 103

5.6 MINTEQ Output File................................ 105

5.7 MINTEQ Zinc Adsorption Input File.................. 112

5.8 MINTEQ Zinc Adsorption Output File................. 114

5.9 Summary of Adsorption Modeling in the White River-Langmuir Constants and Activity Kd for Copper Partitioning........................................ 131

6.1 Ten Mile River Monitoring Stations................. 138

6.2 Ten Mile River Impoundment Monitoring locations.... 139

6.3 Ten Mile River Flow Gaging Stations................ 140

6.4 Ten Mile River Point Source Discharge Monitoring... 141

6.5 Ten Mile River Flows............................... 144

6.6 Ten Mile River Water Quality Data.................. 145

6.7 Ten Mile River Metal Data.......................... 146

6.8 Ten Mile River Copper Loadings - July 1984......... 147

6.9 EXAMS Input - General Data......................... 151

6.10 EXAMS Input - Metal Loading........................ 153

6.11 Ten Mile River Segmentation........................ 155

6.12 MINTEQ Input....................................... 160

6.13 MINTEQ Input for Computing Activity Kd Coefficient. 164

6.14 EXAMS Output - (Table 13).......................... 165

6.15 MINTEQ Output - Percentage Distribution of Components.......................................... 167

6.16 MINTEQ Output - Mass of Dissolved, Precipitated, and Adsorbed Components........................... 168

6.17 Comparison of Predicted and Observed Copper Concentrations...................................... 169

6.18 Typical Speciation of Copper in Ten Mile River..... 171

7.1 Sediment Settling and Resuspension Input........... 177

# ACKNOWLEDGMENTS

The MEXAMS case studies and model testing described in this report were performed under Work Assignment No. 22 of Contract No. 68-03-3116 for the U.S. Environmental Protection Agency, Office of Research and Development. Mr. Lee A. Mulkey and Mr. Robert Ambrose of the Environmental Research Laboratory in Athens, Georgia were the Project Officer and Technical Project Monitor, respectively.

The work was performed by the Palo Alto, CA office of Anderson-Nichols & Co., Inc. and by Ecosystem Research Institute, Logan, Utah. At Anderson-Nichols, Work Assignment 22 was managed by Mr. Brian Bicknell. He conducted the Ten Mile River application; implemented sediment settling and resuspension capabilities in MEXAMS; and authored Sections 3, 6, & 7. Mr. Stuart Brown assisted with project direction and was an invaluable source of advice and information on the model. Dr. Allen J. Medine of Ecosystem Research Institute directed and performed the MEXAMS applications on the White and Naugatuck Rivers, and authored Sections 2, 4 and 5. Dr. Medine and Mr. Bicknell co-authored Sections 1 and 8. Also, Mr. Andrew Felmy, of the University of California, San Diego, provided expert information regarding the theory, application, and coding of MEXAMS.

At Anderson-Nichols, word processing was performed by Ms. Dorothy Inahara and Ms. Mary Maffei; and drafting was provided by Ms. Tomi Hutchins. Incorporation of review comments and development of the final manuscript was performed by these same individuals while employed by AQUA TERRA Consultants, Mountain View, CA, corporate successor to the Palo Alto office of Anderson-Nichols & Co., Inc.

# SECTION 1

# INTRODUCTION

## 1.1 GENERAL

Heavy metals in our aquatic environments, their transport processes, environmental distributions and biological effects have been the focus of increasing concern. Direct toxicity to aquatic organisms and indirect toxicity to higher organisms and man are the center of this concern. Although heavy metals are natural constituents of aquatic environments, additional quantities introduced by man's presence may result in an altered chemical composition of the aqueous and sediment phases, often with detrimental impacts on the environment. In an effort to reduce these impacts, environmental transport/fate models of heavy metals in aquatic ecosystems are being developed.

This study provides a case study testing and tutorial for the Metal Exposure Assessment Modeling System (MEXAMS). This program links MINTEQ, a geochemical model, with the Aquatic Exposure Assessment Model, EXAMS. MEXAMS was developed for the Environmental Protection Agency (EPA) (Felmy et al., 1983) to allow assessment of the impacts of priority pollutant metals (As, Cd, Cu, Pb, Ni, Ag and Zn). The first evaluation consisted of calibrating, testing, and assessing the model response for an actual site application on the Naugatuck River, located in the Housatonic River Basin in western Connecticut.

The second evaluation addressed the use of the MINTEQ geochemical model for the White River, a dynamic lotic system River. This describes the water quality parameter input, laboratory adsorption experiments, chemical analysis, MINTEQ utilization and prediction of laboratory results.

The third evaluation addressed application of MEXAMS to the Ten Mile River, a small stream located in southeastern Massachusetts, which receives inorganic metal waste from numerous industries along its banks. It involved data analysis for a recent data collection program, preparation of detailed MEXAMS input based on the data, and description of the model simulation for purposes of assisting EPA personnel in a wasteload allocation study of the river.

A secondary purpose of this work was to incorporate simple sediment settling and resuspension into MEXAMS. Consideration of metal losses from the water column due to steady-state sediment settling will add an important process to MEXAMS, allowing more accurate calibration and simulation of many systems.

The three case studies comprise the primary results of this study, and are presented in Sections 4, 5, and 6. They are preceded by a brief description of MEXAMS and its component models (Section 2), and an introduction to the complete MEXAMS input, including detailed input preparation guidance for selected MINTEQ options (Section 3). Documentation of the new sediment settling algorithm in MEXAMS is contained in Section 7, and recommendations for future model development and testing are addressed in Section 8.

## 1.2 MODELING POLLUTANT FATE AND TRANSPORT

In the past five years, there has been an increase in the development and use of computer mathematical models to predict the fate and effects of discharged toxic chemicals into the aquatic environment. Many of these models, formulated with the emphasis of predicting site specific effluent load restrictions in accordance with Section 303 of the Clean Water Act, incorporate environmental transport and transformation algorithms. This approach provides more information and understanding of the toxicant's physical-chemical processes (such as bed sediment and suspended solid interactions, bio-availability) than just a total concentration measurement. This understanding of chemical fate and effects can lead to better management of water resources in lieu of man's increasing impact on the environment.

These models are basically general in nature and take on site-specific attributes only by specific input parameters inherent to each model which reflect the system being modeled. The models can vary in complexity, from desk top calculator programs utilizing simplistic first order algorithms, to programs implementing numerical iteration routines in solving the system of differential equations. These programs fall into two basic approach categories; time variable and steady-state.

Time variable models such as WASTOX, TOXIWASP, CHNTRN, TOXIC and TODAM are utilized to model toxic organic distribution in both the water column and sediments, as a function of time. These programs incorporate chemical kinetic routines to account for degradation, transformation, adsorption and desorption. The associated transport algorithms can vary from a one-dimensional compartment to three-dimensional compartment approach. These three-dimensional compartment models utilize hydrodynamic input data for advection, dispersion, compartment volumes, areas and stream velocities. These programs are useful in modeling chemical loading pulses that are not discharged at a continuous rate per time.

Steady-state models are utilized in predicting chemical behavior under constant loading conditions. These models such as SLSA, MICHRIV, CTAP and MEXAMS/EXAMS are more flexible than the time variable models, in the sense that inorganic, as well as organic chemical toxicants can be considered. Like the time variant models, steady-state models vary from one-dimensional to three-dimensional with similar hydrodynamic transport routines.

In considering the modeling of inorganic heavy metals, only MEXAMS accounts for chemical speciation, dissolved, adsorbed and precipitated metal concentrations. MEXAMS is the coupling of two existing computer programs; MINTEQ a geochemical steady-state equilibrium model, and the migration and fate portions of the EXAMS model. This coupling provides the capability to predict quantities of dissolved metal in the aquatic system and ascertain the effect of chemical speciation related to solid phase partitioning and chemical precipitation.

MEXAMS, as with other complex, site-specific programs, requires extensive input parameters obtained through laboratory experimentation and analysis along with field hydrodynamic, physical and chemical data.

# SECTION 2

# MODEL DESCRIPTIONS

## 2.1 EXAMS GENERAL DESCRIPTION

The Exposure Assessment Model System (EXAMS) was developed in response to a need to describe fate, transport and impacts of organic contaminants in aquatic systems. The program is a deterministic, predictive systems model, based on a core of mechanistic process equations derived from fundamental theoretical concepts (Burns et al., 1982).

The model estimates exposure, fate, and persistence of organic pollutant discharges. Exposure is defined as the steady-state pollutant concentration after loadings are balanced with transport and transformation processes. Fate is defined as the distribution of the pollutant in the system, and persistence is the time required for effective purification of the system. The program uses conservation of mass to balance loadings, transport and transformation of the compound.

The chemical loadings can be entered into EXAMS by way of:

1. Point Source Loadings
2. Non-Point Source Loadings
3. Aerial Drift
4. Atmospheric Washout
5. Groundwater Seepage

These chemicals can then be transformed by photolysis, hydrolysis, biochemical and oxidation reactions in particular compartments of the environment under simulation. In addition to the above transformation processes, EXAMS is capable of three transport processes: advection (dependent on the hydrologic data input), dispersion (dependent on the description of each dispersive pathway) and volatilization (the air/water interface). Advective and dispersive transport are possible for dissolved species, sediment sorbed material and bio-sorbed materials. Transport through the ecosystem compartments may be represented by whole sediment bed loads, suspended sediment washloads, exchanges with fixed volume sediment beds and ground water infiltration.

EXAMS can also be used to simulate the ionization and sorption of up to fifteen molecular species of an organic chemical. The chemical can be the parent uncharged, singly or doubly charged cations and anions, each of which can occur in the dissolved, sediment-sorbed or bio-sorbed forms. However, EXAMS, like all models, contains important assumptions. These assumptions are listed as follows:

1. A first order evaluation can be executed independently of the chemicals actual effects on the system,
2. Linear sorption isotherms and second order expressions are used, rather than Michaelis-Menten-Monod expressions, for biolysis,
3. EXAMS was developed for long-term or steady-state loadings rather than dynamic transitory (spills) loadings, and
4. Sorption is treated as an equilibrium process, that is, adsorption/desorption are assumed to be rapid compared to other processes.

EXAMS is capable of simulating both lotic and lentic aquatic systems. These systems are initially compartmentalized and classified as littoral, epilimnion, hypolimnion or benthic (Figure 2.1 illustrates compartmentalization of a lake system and a river system). Each compartment is assumed to be completely mixed. The computer then develops single differential equations for each compartment. The form of the equation and the variables are defined as:

$$V \frac{dc}{dt} = L_e + L_i - VKC \qquad (2.1)$$

where $V$ = volume of water in compartment (l)
$C$ = total chemical concentration in compartment (mg/l)
$L_e$ = total external loading (mg\hr)
$L_i$ = total internal loading (mg\hr)
$K$ = overall pseudo-first order loss constant (/hr)
$t$ = time

EXAMS was not originally designed to describe metal transport and fate and has been modified so that it can interface with MINTEQ. The first modification involved bypassing calculations that are unnecessary for heavy metal speciation or duplicated by MINTEQ. The second modification included provisions for describing migration and fate of precipitated

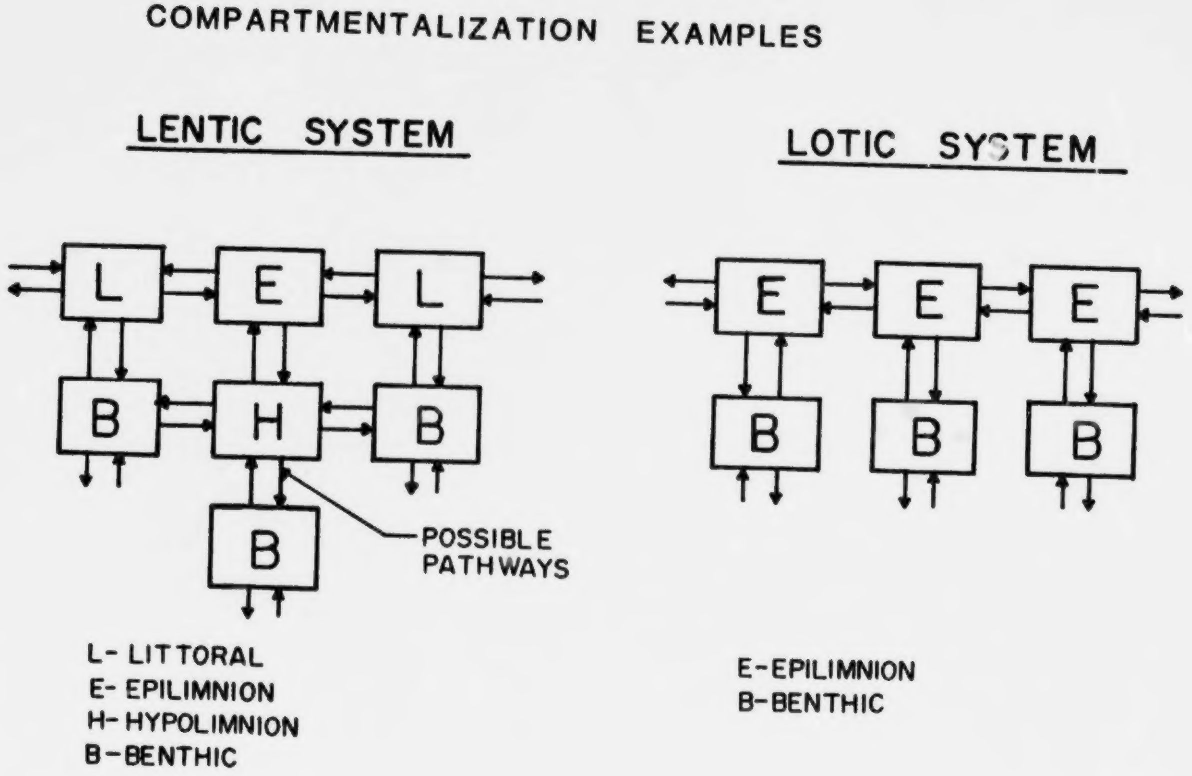

COMPARTMENTALIZATION EXAMPLES
LENTIC SYSTEM
LOTIC SYSTEM
L
E
L
B
H
B
B
POSSIBLE PATHWAYS
L- LITTORAL
E- EPILIMNION
H- HYPOLIMNION
B-BENTHIC
E
E
E
B
B
B
E-EPILIMNION
B-BENTHIC

Figure 2.1 Compartmentalization examples.

fractions. Ionization is not utilized in MEXAMS, because MINTEQ calculates dissolved species in each compartment. Finally, priority metals are generally unaffected by the transformation and degradation processes that affect the fate of organics in natural waters, and these processes are bypassed in the modified EXAMS version.

## 2.2 MINTEQ GENERAL DESCRIPTION

MINTEQ is a computer program for calculating aqueous geochemical equilibria and was developed for incorporation into MEXAMS. The major objective of MINTEQ is the development of a predictive methodology for the assessment of the metal speciation including sorption, precipitation and ion exchange of priority pollutant metals in aquatic environments. This chemical equilibrium problem is described as a set of mass balance equations, one for each component, and a set of mass action equations, one for each specie. The equilibrium constant approach is utilized to solve the equilibrium problem. This method solves nonlinear mass action expressions using linear mass balance equations. The equilibrium composition of an aquatic environment is determined by minimization of Gibbs free energy of the system within the mass balance constraints. This chemical equilibrium will determine aqueous metal speciation in addition to the effects of precipitation/dissolution and sorption, and is used in EXAMS to determine the metal fate and migration. The typical mass action and mass balance equations are as follows:

Mass Action:

$$v_i \; C_i = K_i \prod_{j=1}^{n} X_j^{a(i,j)} \qquad (2.2)$$

where $v_i$ = activity coefficient of species i
$C_i$ = concentration of species i
$K_i$ = equilibrium constant reaction i
$X_j$ = activity of component j
$a(i,j)$ = stoichiometric coefficient of components in species i
$n$ = number of components

Mass Balance:

$$T_j = \sum_{j=1}^{m} a(i,j) \; C_i \qquad (2.3)$$

where $T_j$ = total analytical concentration of component j
$m$ = number of aqueous species

Both of the above equations are definitions for systems with no solid phases. Solid phases are dealt with using the "transformation of basis" method (Felmy et al., 1984a). This method reduces the number of independent variables to be determined and allows the solution of a wider range of chemical equilibrium problems.

MINTEQ is also capable of modeling adsorption in a number of ways. Six different algorithms are accessible through the use of MINTEQ for describing sorption phenomena:

1. "activity" Kd
2. "activity" Langmuir equation
3. "activity" Freundlich equation
4. ion exchange
5. constant capacitance surface complexation model
6. triple layer surface complexation model

The "activity" Kd approach is the ratio of the adsorbed metal concentration to the solution metal concentration (activity of the free ion). The Kd equation can then be written as follows:

$$K_d = \frac{CuS}{\{Cu^{+2}\}} \qquad (2.4)$$

where $K_d$ = distribution coefficient
$CuS$ = particulate concentration (molal units)
$\{Cu\}$ = activity concentration of the free metal (molal units)

The "activity" Langmuir equation has an advantage over the Kd approach, because a mass balance on surface sites is considered. The "activity" Langmuir equation is written as follows:

$$CuS = \frac{K_L\, S_t\, \{Cu^{+2}\}}{1 + K_L\, \{Cu^{+2}\}} \qquad (2.5)$$

where $S_t$ = maximum quantity that can be adsorbed
$K_L$ = Langmuir adsorption constant

The third approach, the "activity" Freundlich, can also describe adsorption data and, in many cases, is used when laboratory data obtained does not conform to the "activity" Langmuir. The "activity" Freundlich equation is written as follows:

$$CuS = K_f \{Cu^{+2}\}^{1/n} \tag{2.6}$$

where $K_f$ = Freundlich adsorption constant
$n$ = a constant

The above three activity approaches are preferred over the concentration counterparts because it is currently hypothesized that only certain aqueous species react with the absorbing surface, as opposed to assuming that all aqueous species absorb with equal strength. Using the free ion in the activity approaches allows the model to deal with a wider range of natural waters with different degrees of inorganic and organic complexation. However, the activity approach is not without limitations. The activity approach does not charge balance surface sites and adsorbed species. Secondly, electrostatic interactions between adsorbing ion and charged surfaces are not considered. Finally, the reaction of solid with aqueous constituents other then adsorbate ion is not considered. In order to reduce the above limitations, surface complexation models have been developed which may be more applicable, but also more complex (Felmy et al., 1984a).

The constant capacitance model and triple layer models, both based on theoretical approaches, consider charge potential differences and changing properties of the surface with changing pH and ionic strength. Both of these methods require a great deal of detailed laboratory investigation to determine the critical parameters and are primarily research tools.

The ion exchange approach is only useful when the selectivity coefficients for the exchange reactions are known. These coefficients are generally only available for bulk electrolyte ions such as Na+, K+, and Ca+2. The ion exchange model is less useful for predicting metal adsorption, because metal adsorption is most likely the result of covalent bonds with surface sites (Felmy et al., 1984a).

## 2.3 MEXAMS GENERAL DESCRIPTION

The two previous sections described the two individual models that have been linked to form the MEXAMS model (Figure 2.2). The MEXAMS program can be used in both batch and interactive mode with three different modes of operation available.

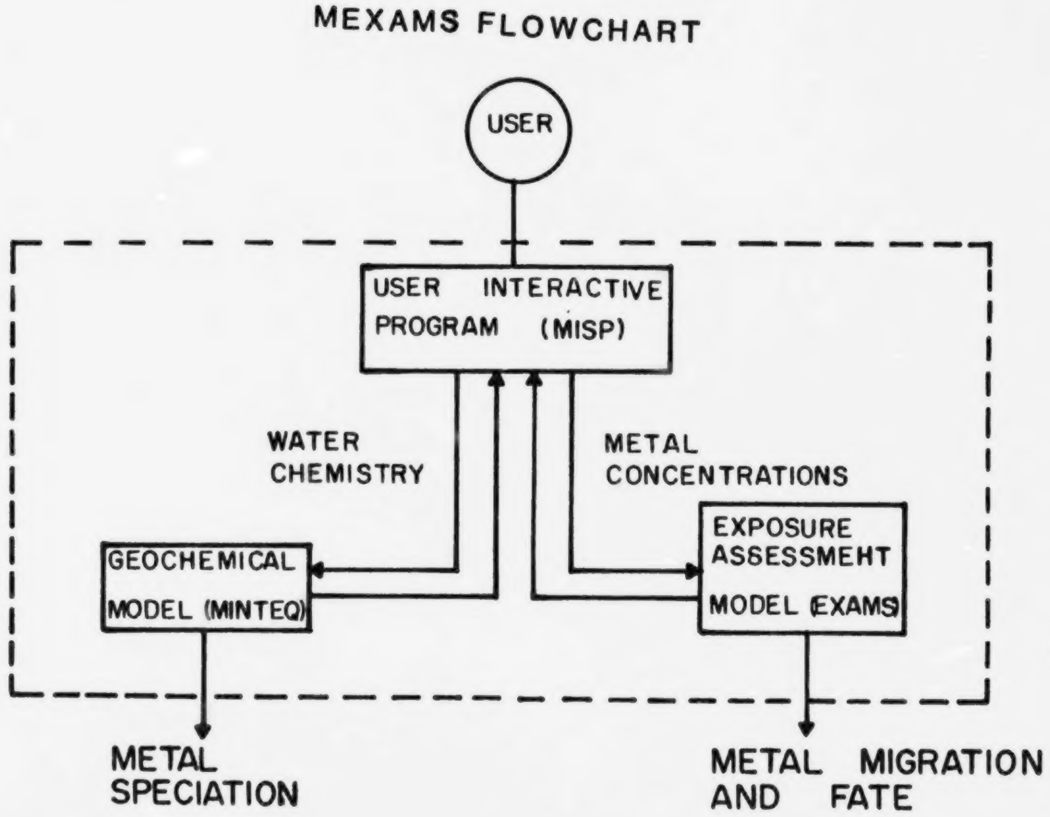

MEXAMS FLOWCHART
USER
USER INTERACTIVE PROGRAM (MISP)
WATER CHEMISTRY
METAL CONCENTRATIONS
GEOCHEMICAL MODEL (MINTEQ)
EXPOSURE ASSESSMEHT MODEL (EXAMS)
METAL SPECIATION
METAL MIGRATION AND FATE

Figure 2.2  MEXAMS flowchart.

The first mode is the MINTEQ only, which allows the operator to determine how changes in water chemistry will affect metal speciation and solid phase interactions without regard to transport processes. Secondly, the EXAMS only mode, which deals with the ionization, sorption, transport and transformation of a given pollutant. Finally, the third mode, which links EXAMS and MINTEQ together, allows the user to determine the effect of transport processes and chemical interactions on priority pollutant concentration. This section will describe the operation and use of the coupled mode.

The first step is to create an EXAMS input file that describes the characteristics of the aquatic environment being assessed. The user then enters the MEXAMS Interactive Software Package (MISP). MISP will call for a MINTEQ file for each compartment that contains different water quality data. The programmer will also input run-specific information that controls the number of times MINTEQ updates metal concentrations. MEXAMS is now set to simulate metal behavior, migration and fate.

Initial calculations by EXAMS are made without using MINTEQ (i.e. assuming no adsorption or precipitation) and the initial distribution of dissolved metals in each compartment is obtained. These concentrations, along with suspended sediment and biota concentrations, are sent on to MISP. MISP then passes the dissolved metal concentration in the first compartment on to MINTEQ, which simultaneously reads the water quality data for that compartment. MINTEQ then improves the estimate of the concentration of metal in solution, adsorbed to sediments and biota and in a precipitated form. These results are returned to MISP and metal fractions are determined.

MISP then proceeds to the second compartment and, unless the water quality is different and the total metal varies by more than 5%, MINTEQ is not called. MISP utilizes the same fractions from the previous compartment. If total metal varies by more than 5%, MINTEQ is called, but an entire new calculation is only performed when the water quality data differs from one compartment to the next.

After metal fractions have been computed for all compartments, MISP sends the information to EXAMS and the metal transport and transformation are computed. EXAMS then predicts new exposure levels and iterates with MINTEQ again. Calculations of fate and persistence are performed until all iterations are complete.

The MEXAMS computer program is capable of solving a wide variety of pollution problems. A list of possible uses follows:

1. Rapid evaluation of synthetic organic pollutants
2. Rapid hazard evaluation for priority pollutant metals
3. Assess impact of point source discharge from mine drainage
4. Provide support and interpretations of metals bioassays
5. Provide a Framework for what is or what is not known about the behavior of priority pollutant metals in aquatic systems
6. As a Management tool

# SECTION 3

# MEXAMS INPUT AND USER GUIDANCE

This section provides a brief overview of all of the input requirements of MEXAMS, and detailed descriptions of the MINTEQ input necessary to implement several of the optional adsorption models. Since the use of EXAMS and its input requirements are fully documented and detailed in the EXAMS user's manual (Burns et al., 1982), this section is intended to introduce the user to the subset of EXAMS input required by MEXAMS, and to provide guidance in planning a MEXAMS application and data collection activities. MINTEQ is a newer, less documented model, and relatively untested compared with EXAMS. Furthermore, MINTEQ input for various options and applications is more complex, especially to those unfamiliar with chemical equilibrium/speciation models. We concluded that detailed guidance on these options would be beneficial to future users. In summary, this section is intended to supplement the existing MEXAMS documentation (Felmy et al., 1984a, 1984b) by (1) providing an overview of the EXAMS input required by MEXAMS, and (2) giving the user specific guidance in setting up some of the more complicated types of MINTEQ input. This guidance is written with the idea that it may be incorporated into a future MEXAMS documentation package which also includes case studies.

## 3.1 EXAMS INPUT

EXAMS input required by MEXAMS are contained in two of the usual EXAMS input files. These are the "user run information" file consisting of chemical loadings to each of the ecosystem compartments, and the "environmental data" file consisting of a complete description of the ecosystem. As a compartmental model, EXAMS requires data such as the physical dimensions, flows, sediment loading, and other characteristics describing each of the compartments, and also parameters which define the connections between these compartments. The latter includes advective, dispersive, and sediment settling/resuspension pathways. Tables 3.1 and 3.2 list and define the necessary EXAMS inputs for MEXAMS. (Other parameters must have "dummy"

## TABLE 3.1 EXAMS INPUT PARAMETERS DESCRIBING ECOSYSTEM COMPARTMENTS AND EXTERNAL LOADINGS

| Name | Definition | Units |
|---|---|---|
| I | Number of metal loadings defined | - |
| STRLDG,NPSLDG,etc. | Metal loadings (to specified compartment) in stream flow, non-point source flows, etc. | kg/hr |
| KOUNT | Number of compartments in the ecosystem | - |
| TYPEE | Compartment types (L,H,E,B) | - |
| VOLG | Volumes of compartment | m |
| AREAG | Surface areas of compartments | m2 |
| DEPTHG | Depths of compartments | m |
| STFLOG | Flows entering compartments from tributaries, waste flows, etc. | m3/hr |
| STSEDG | Sediment loadings associated with STFLOG | kg/hr |
| NPSFLG | Non-point source flows entering compartments | m3/hr |
| NPSFDG | Sediment loadings associated with NPSFLG | kg/hr |
| INTFLG | Interflow entering compartments | m3/hr |
| RAING | Rainfall rate | mm/mo |
| EVAPG | Evaporation rate | mm/mo |
| SDCHRG | Sediment concentrations<br>water column:<br>benthic (bulk density): | <br>mg/l<br>g/cm3 |
| PCTWAG | Percent water in benthic compartments; (100. * fresh wt./dry wt. of sediment) (> 100%) | % |

## TABLE 3.2 EXAMS INPUT PARAMETERS DESCRIBING COMPARTMENT INTERCONNECTIONS

| Name | Definition | Units |
|---|---|---|
| NSPEC1 | Number of advective connections | - |
| JFRADG | Source compartment numbers for advective flow connections | - |
| ITOADG | Receiving compartment numbers for advective flow connections | - |
| ADVPRG | Fraction of advective flow leaving compartment JFRADG which is delivered to compartment ITOADG | - |
| NSPEC2 | Number of dispersive connections | - |
| JTURBG, ITURBG | Source and receiving compartment numbers defining dispersive connections | - |
| XSTURG | Cross-sectional area of dispersive connection defined by JTURBG,ITURBG | m2 |
| CHARLG | Characteristic legth for dispersive connection defined by JTURBG,ITURBG | m |
| DSPG | Eddy diffusivity for dispersive connection defined by TURBG,ITURBG | m2/hr |
| NSPEC3 | Number of sediment settling/ resuspension connections | - |
| JSETLG,ISETLG | Source and receiving compartment numbers defining settling/ resuspension connections | - |
| SETLRG | Sediment settling rate for connection defined by JSETLG,ISETLG | m/hr |
| RSUSPG | Sediment resuspension rate for connection defined by JSETLG,ISETLG | mm/yr |
| XSSETG | Cross-sectional area of connection defined by JSETLG,ISETLG | m2 |

values). Table 3.1 consists of the data describing compartment dimensions and loading, while Table 3.2 contains the compartment connectivities and related parameters. The user should refer to the EXAMS User's Manual (Burns et al., 1982) for input formats and more detailed guidance on input parameter definition, estimation, and restrictions. Section 7 of this document currently provides the documentation for sediment settling/resuspension, since those capabilities were added to MEXAMS recently, and are not available in the standard EXAMS model for organic contaminants.

The hydraulics calculations performed by EXAMS are relatively unsophisticated. They rely on a complete understanding of flow routing and travel times to obtain reasonable estimates of pollutant transport. Consequently, the principal inputs are compartment volumes and streamflows. Generally, this requires detailed knowledge of the depths, widths, and flows over the length of the stream. In addition, it is often valuable to compare observed travel times with those computed from flow and cross-sction data in order to "calibrate" the system. However, those data are not necessary.

EXAMS sediment transport calculations are also fairly simple. Adsorbed metal concentrations and transport are determined from the sediment concentrations (water column) and bulk densities (benthic) which are required input parameters. Sediment loading to the ecosystem, while required input, is not actually used by the metals version of EXAMS.

Metal loadings to each compartment are included in the EXAMS input. The user may specify separate loadings from point source discharges, non-point sources, tributary inflow, and ground-water inflow. The reader should note that MEXAMS considers the transport of only one metal at a time, and this metal is referred to as "the metal being followed". All chemical/adsorption characteristics associated with this metal (as well as other metals) are defined in the MINTEQ input and MINTEQ data base; however, loadings of this metal to the system are included in the EXAMS input.

EXAMS computations also require the explicit definition of flow pathways or connectivity of the compartments in the system. Allowed pathways or flows in EXAMS are advection, dispersion, and sediment settling/resuspension. (This last pathway type is currently available only in the MEXAMS version of EXAMS on IBM computers). Advective convections require specification of compartment pathways and the fraction of flow along each pathway. Dispersion and settling/resuspension convections are characterized via cross sectional area, dispersion, coefficients, and settling rates as well as the connected compartment numbers.

## 3.2 MINTEQ INPUT

The MINTEQ input is described and documented in detail in Section 6 and Appendix C of the MEXAMS user manual (Felmy et al., 1984b). The user should be familiar with much of the information presented in those sections since the following discussion assumes a basic understanding of the MINTEQ input.

The MINTEQ input is separated into three sections as follows:

1. Basic Input Data - consists of alphanumeric descriptions, water temperature, analytical unit system, various option flags, adsorption data, and chemical "components" considered in the simulation along with their measured concentrations;

2. Type Modifications - default species type designations and default equilibrium constants can be overridden in order to effect a particular option; for example, input in this section would be used to specify a fixed pH or a gas at a fixed partial pressure or to limit the solids considered in the problem to a preselected set.

3. Insertion of New Species - new chemical species, such as adsorbed metal complexes, are defined and characterized by appropriate stoichiometry and equilibrium constant.

The program has the capability of managing six different species types (Felmy et al., 1984b). The Type I species are components that are used to define the chemical constituents that make up the water quality matrix. Type II species are complexes which are combinations of two or more components. These Type II species are not a routine user input but instead are determined by MINTEQ, utilizing the thermodynamic data base of the Type I species inputted. Type III specification is given to species with fixed activities such as pH or PE solid phases present in infinite supply (solids), gases present at fixed partial pressures and redox reactions between components. Type IV species are precipitated solids (of finite mass) that are subject to dissolution. Type V species are dissolved solids subject to precipitation when saturated indices are exceeded. Type VI species are species not considered during the equilibrium calculations (solids and complexes). Instead, these species are considered after equilibrium calculations are completed.

Generally, the input in each of these sections is well described in the users manual, and is straight forward for simple applications of the program, such as those in which adsorption is unimportant and relatively few chemical species are present. Many applications and options require more complex input and also require interaction between the three sections; consequently, the input becomes less straightforward to implement for the novice user. Furthermore, explanations of the input are located in several different sections of the documentation. We concluded that additional detailed operational instructions would be helpful. The options which are presented in this document are the following adsorption models:

- Activity Kd Adsorption
- Activity Langmuir Adsorption
- Triple-Layer Surface Complexation (Adsorption)

### 3.2.1 Activity Kd Adsorption

The equilibrium adsorption model (Kd) incorporated in MINTEQ differs from a standard Kd in two ways. First, the MINTEQ Kd model assumes that only the uncomplexed metal ion adsorbs to solid rather than all dissolved aqueous complexes. Thus, the Kd must be calculated using the activity of the metal species in solution. The Kd becomes Kd-activity, and is defined by the following expression:

$$\mathrm{Kd(act)} = \frac{[M^{+2}]_{ads}}{\{M^{+2}\}_{aq}} \qquad (3.1)$$

where $[M^{+2}]$ads = the concentration of metal ion in the system which is adsorbed (mole/l)

$\{M^{+2}\}$aq = activity of free metal ion in the system (mole/l)

The second difference from a standard Kd model is that the MINTEQ Kd assumes that the solids concentration is in excess and its activity or concentration is 1. Thus, the simulated concentration of adsorbed metal will not vary as a function of suspended solids concentration. Another way of looking at this difference is to consider the standard expression for Kd:

$$\mathrm{Kd(std)} = \frac{[M^{+2}]_{ads}/S}{\{M^{+2}\}_{aq}} \qquad (3.2)$$

where S = concentration of suspended solids (kg/l)
$[M^{+2}]$aq = total concentration of dissolved metal species in system (mole/l)

If we assume that $\{M^{+2}\}$aq = $[M^{+2}]$aq and substitute Equation 3.1 into 3.2 we find that:

$$Kd(act) = Kd(std) \cdot S \qquad (3.3)$$

The result of this is that the input Kd in MINTEQ is a function of solids concentration and should be recalculated by the user for each compartment where this value changes. With the above differences in mind, the activity Kd model is implemented through the following procedure:

1. Make a preliminary MINTEQ run to simulate the solution from which the standard Kd was obtained; include the complete chemical analysis of the water sample, including the dissolved metal ion concentration. Table 3.3 presents a simple example of the MINTEQ input for these runs.

2. Compute the activity Kd from Equation 3.1, where $\{M^{+2}\}$aq is the activity of the uncomplexed metal computed in the above MINTEQ run and $[M^{+2}]$ads is the measured concentration of adsorbed metal.

3. Subsequent MEXAMS model runs in which this activity Kd model is used must contain the information listed below (An example is shown in Table 3.4):

    a) adsorption flag = 1; all other inputs on the "adsorption" input line are 0

    b) include the metal and SOH1 as components (with concentrations of 0)

    c) change the type of SOH1 to Type III (fixed)

    d) include "SO-M" as a new Type II species (aqueous complex) with the equilibrium constant equal to Kd-activity and correct stoichiometry

It should be emphasized that the MINTEQ inputs shown in Tables 3.3 and 3.4 are examples only, and are not applicable to all "Kd" situations. Each particular application will require a unique input sequence.

## TABLE 3.3 EXAMPLE MINTEQ INPUT TO COMPUTE ACTIVITY Kd

```
MINTEQ RUN TO COMPUTE FREE METAL ACTIVITY FOR Kd or KL
APRIL 18, 1984
20.00 MG/L     0.00
1 0 1 1 2 0 0 0
0   0.00    0.00    0.00    0.00
    140 2.800E+01    0.00
    330 0.000E+01   -6.50
    732 3.500E+00    0.00
    150 1.300E+01    0.00
    460 2.000E+00    0.00
    280 1.400E-01    0.00
    600 3.000E-02    0.00
    540 3.000E-02    0.00
    231 2.333E-02    0.00
    950 1.000E-02    0.00
    492 8.000E+00    0.00
    580 7.000E-01    0.00
    180 2.200E+01    0.00
    500 2.000E+01    0.00
    410 1.000E+00    0.00
    490 7.000E-02    0.00

  3   1
    330 6.500E+00    0.00
```

## TABLE 3.4 EXAMPLE MINTEQ INPUT TO SIMULATE ACTIVITY Kd ADSORPTION

```
MINTEQ RUN TO SIMULATE ACTIVITY Kd ADSORPTION
APRIL 18, 1984 - COPPER IN REACH 1
20.00 MG/L    0.00
1 0 1 1 2 0 0 0
1   0.00   0.00   0.00   0.00
    140 2.800E+01   0.00
    330 0.000E+01  -6.50
    732 3.500E+00   0.00
    150 1.300E+01   0.00
    460 2.000E+00   0.00
    280 1.400E-01   0.00
    600 3.000E-02   0.00
    231 0.000E-00   0.00
    950 1.000E-02   0.00
    990 0.000E-00   0.00

  3   2
    330 6.500E+00   0.00
    990 0.000E+00   0.00

  2   1
9902310 SOH1-CU                   1.1200
           1.00 231    1.00 990
```

### 3.2.2 Activity Langmuir Isotherm Adsorption

The activity Langmuir is preferable to the activity Kd model because it considers the effects of variable metal concentrations, and it considers a mass balance on surface sites (i.e. solids concentration). However, more detailed experimental data are required to implement the activity Langmuir isotherm. It is necessary to simulate the water samples used in the laboratory determination of the standard Langmuir isotherm to obtain the activity of the uncomplexed metal ion. The isotherm is then redrawn to obtain the "activity" Langmuir K and the total surface sites. Finally, the new isotherm, along with the appropriate stoichiometric information for the adsorption reaction, is used to represent adsorption in MINTEQ or MEXAMS model runs. The following is an outline of the procedure:

1. Make preliminary MINTEQ runs to simulate each of the water samples which were analyzed to determine the standard Langmuir isotherm. MINTEQ input for these runs will consist of the basic water quality analyses, i.e., component concentrations (including metals), pH, etc. Since these simulations are identical to those for determining the activity Kd, Table 3.3 is an example.

2. Replot the isotherm using the computed activity of the uncomplexed metal ion; i.e., plot $\{M^{+2}\}/S$ versus $\{M^{+2}\}$. Obtain the "activity" $K_L$ and $S_T$ in the usual fashion.

3. Subsequent MEXAMS or MINTEQ model runs in which this activity Langmuir model is used must include the following information (an example is shown in Table 3.5):

    a) adsorption flag = 1; all other inputs on the "adsorption" input line are 0;

    b) include the metal and SOH1 as components; set their analytical concentrations to 0, and S respectively;

    c) include "SO-M" as a new type II species with the equilibrium constant equal to $K_L$ (activity) and the appropriate stoichiometry.

TABLE 3.5 EXAMPLE MINTEQ INPUT TO SIMULATE ACTIVITY $K_L$ ADSORPTION

```
MINTEQ RUN TO SIMULATE ACTIVITY KL ADSORPTION
APRIL 18, 1984 - COPPER IN REACH 1
20.00 MG/L    0.00
1 0 1 1 2 0 0 0
1   0.00   0.00   0.00   0.00
    140 2.800E+01   0.00
    330 0.000E+01  -6.50
    732 3.500E+00   0.00
    150 1.300E+01   0.00
    460 2.000E+00   0.00
    280 1.400E-01   0.00
    600 3.000E-02   0.00
    231 0.000E-00   0.00
    950 1.000E-02   0.00
    990 1.500E+01   0.00

  3   1
    330 6.500E+00   0.00

  2   1
9902310 SOH1-CU                  6.9000
           1.00 231    1.00 990
```

### 3.2.3 Triple-Layer Surface Complexation

Data requirements and operational procedures for the two surface complexation adsorption models are much greater than the Kd and Langmuir isotherm formulations. The data and procedures used to implement the triple-layer model are described here in some detail; procedures for the constant capacitance model are similar. First, this discussion itemizes data needs, and second, the operational procedures for executing the model are described. Much of this information is already presented in the MEXAMS documentation; however, it is located partially in the MINTEQ reference document (Felmy et al., 1984a) and partially in the MEXAMS user's guide (Felmy et al., 1984b).

Generally, users of the surface complexation models will be familiar with the pioneering work in this field by Leckie and co-workers at Stanford University, as well as related literature. References of note are Davis et al. (1978), Davis and Leckie (1978, 1980), Benjamin and Leckie (1982), and Balistrieri and Murray (1981, 1982). For systems where the primary adsorbents are single oxides and mixtures of oxides, these references provide valuable sources of data and insight required to intelligently use the surface complexation models in MINTEQ. However, more information is necessary for application to systems where the adsorbent is primarily soil or sediment. Future development of field/laboratory procedures for collection of these data is needed.

Data Requirements

1. Concentration of solid absorbent (g/l)

2. Specific surface area of the adsorbent (m2/g) Literature values for various metal oxide adsorbents are available (Davis and Leckie, 1978).

3. Specific surface site density of adsorbent (sites/g). Davis and Leckie (1978) list data for single oxides

4. Inner and outer layer capacitances (Farads/m2). The MINTEQ documentation recommends 1.4 and 0.2 Farads/m2, respectively for these parameters.

5. Potentials at surface, beta, and diffuse planes (dimensionless). The MINTEQ documentation recommends guesses between -0.2 and -4.0 for each of these parameters.

6. Equilibrium constants and stoichiometry data for surface hydrolysis reactions. These data represent

the actual adsorption reactions of various solutes to the solid surface sites. The previously referenced literature contains this information for a number of hydrous oxides and other solids. Felmy (personal communication) has compiled the reaction data for a number of species adsorbing to iron oxyhydroxide in the proper format for input to MINTEQ. The reaction stoichiometry and constants are presented in Table 3.6 as a resource to those interested in adsorption on this solid, and as a guide for other oxide systems.

Operational Procedures

1. Include SOH1, XPSIO, XPSIB, and XPSID as components. The corresponding input field for component analytical concentration should contain the surface site density (item 3 above) for SOH1, and the initial guesses for the three potentials (item 5 above).

2. The adsorption flag = 3; the remaining four parameters on the adsorption line are items 1, 2, and 4 above.

3. Change the types of the potentials to Type VI.

4. Include in the database all of the new species implied by the surface hydrolysis reactions. The reactions shown in Table 3.6 above, are included in an example MINTEQ input sequence (Table 3.7) for the triple-layer model.

TABLE 3.6 SURFACE REACTIONS FOR THE TRIPLE-LAYER MODEL ON AMORPHOUS IRON OXYHYDROXIDE

| Reaction Stoichiometry | Log K |
|---|---|
| $SOH \rightleftharpoons SO^{-} + H^{+}$ | -10.7 |
| $SOH + H^{+} \rightleftharpoons SOH2^{+}$ | 5.1 |
| $SOH + Na^{+} \rightleftharpoons SO\text{-}Na + H^{+}$ | -9.0 |
| $SOH + NO3^{-} + H^{+} \rightleftharpoons SOH2\text{-}NO3$ | 6.9 |
| $SOH + SO4^{-2} + H^{+} \rightleftharpoons SOH2\text{-}SO4^{-}$ | 9.90 |
| $SOH + SO4^{-2} + 2H^{+} \rightleftharpoons SOH2\text{-}HSO4$ | 15.9 |
| $SOH + K^{+} \rightleftharpoons SO\text{-}K + H^{+}$ | -8.4 |
| $SOH + Mg^{+2} \rightleftharpoons SO\text{-}Mg^{+} + H^{+}$ | -5.45 |
| $SOH + Mg^{+2} + H2O \rightleftharpoons SO\text{-}MgOH + 2H^{+}$ | -14.25 |
| $SOH + Ca^{+2} \rightleftharpoons SO\text{-}Ca^{+} + H^{+}$ | -5.00 |
| $SOH + Ca^{+2} + H2O \rightleftharpoons SO\text{-}CaOH + 2H^{+}$ | -14.50 |
| $SOH + Cl^{-} + H^{+} \rightleftharpoons SOH2\text{-}Cl$ | 7.00 |
| $SOH + Cd^{+2} \rightleftharpoons SO\text{-}Cd^{+} + H^{+}$ | -4.90 |
| $SOH + Cd^{+2} + H2O \rightleftharpoons SO\text{-}CdOH + 2H^{+}$ | -11.0 |
| $SOH + Pb^{+2} \rightleftharpoons SO\text{-}Pb^{+} + H^{+}$ | -3.80 |
| $SOH + Pb^{+2} + H2O \rightleftharpoons SO\text{-}PbOH + 2H^{+}$ | -7.30 |
| $SOH + Cu^{+2} \rightleftharpoons SO\text{-}Cu^{+} + H^{+}$ | -4.10 |
| $SOH + Cu^{+2} + H2O \rightleftharpoons SO\text{-}CuOH + 2H^{+}$ | -9.00 |
| $SOH + Zn^{+2} + H2O \rightleftharpoons SO\text{-}ZnOH + 2H^{+}$ | -9.60 |

Source: A. Felmy (personal communication)

# TABLE 3.7 MINTEQ INPUT TO SIMULATE TRIPLE-LAYER SURFACE COMPLEXATION

```
TRIPLE-LAYER ADSORPTION
APRIL 18, 1984 - CU IN REACH 1
20.00 MG/L    0.00
1 0 1 1 2 0 0 0
3   4.00   600.   1.40   0.20
    140 2.800E+01   0.00
    330 0.000E+01  -6.50
    732 4.500E+00   0.00
    150 1.300E+01   0.00
    460 2.000E+00   0.00
    180 1.400E-01   0.00
    600 3.000E-02   0.00
    410 2.000E+00   0.00
    492 7.500E+00   0.00
    500 3.000E+01   0.00
    950 1.000E-01   0.00
    160 1.600E-01   0.00
    231 0.000E-00   0.00
    990 5.500E+21   0.00
    992 0.000E-00  -2.00
    993 0.000E-00  -2.00
    994 0.000E-00  -2.00

  3   1
    330 6.500E+00   0.00
  6   3
    992 0.000E+00   0.00
    993 0.000E+00   0.00
    994 0.000E+00   0.00

  2  19
9903300 SO-                0.0     -10.7
  0.0 3       1.0 990    -1.0 330    -1.0 992

9903301 SOH2+              0.0       5.1
  0.0 3       1.0 990     1.0 330     1.0 992

9905000 SO-NA              0.0      -9.0
  0.0 5       1.0 990     1.0 500    -1.0 330    -1.0 992     1.0 993

9904920 SOH2-NO3           0.0      6.90
  0.0 5       1.0 990     1.0 330     1.0 492     1.0 992    -1.0 993

9907320 SOH2-SO4           0.0     -9.90
  0.0 5       1.0 990     1.0 732     1.0 330     1.0 992    -2.0 993

9907321 SOH2-HSO4          0.0      15.9
  0.0 5       1.0 990     1.0 732     2.0 330    -1.0 993     1.0 992

9904100 SO-K               0.0      -8.4
  0.0 5       1.0 990     1.0 410    -1.0 330    -1.0 992     1.0 993

9904600 SO-MG+             0.0     -5.45
  0.0 5       1.0 990     1.0 460    -1.0 330    -1.0 992     2.0 993

9904601 SO-MGOH            0.0    -14.25
  0.0 6       1.0 990     1.0 460     1.0 002    -2.0 330    -1.0 992     1.00 993

9901500 SO-CA+             0.0     -5.00
  0.0 5       1.0 990     1.0 150    -1.0 330    -1.0 992     2.0 993

9901501 SO-CAOH            0.0    -14.50
  0.0 6       1.0 990     1.0 150     1.0 002    -2.0 330    -1.0 992     1.00 993

9901800 SOH2-CL            0.0      7.00
  0.0 5       1.0 990     1.0 180     1.0 330     1.0 992    -1.0 993

9901600 SO-CD+2            0.0     -4.90
  0.0 5       1.0 990     1.0 160    -1.0 330    -1.0 992     2.0 993

9901601 SO-CDOH+           0.0     -11.0
  0.0 6       1.0 990     1.0 160     1.0 002    -2.0 330     1.0 993    -1.00 992

9906000 SO-PB+             0.0     -3.80
  0.0 5       1.0 990     1.0 600    -1.0 330    -1.0 992     2.0 993

9906001 SO-PBOH+           0.0     -7.30
  0.0 6       1.0 990     1.0 600     1.0 002    -2.0 330     1.0 993    -1.00 992

9902310 SO-CU+2            0.0     -4.10
  0.0 5       1.0 990     1.0 231    -1.0 990    -1.0 992     2.0 993

9902311 SO-CUOH+           0.0     -9.00
  0.0 6       1.0 990     1.0 231     1.0 002    -2.0 330     1.0 993    -1.00 992

9909500 SO-ZNOH+           0.0     -9.60
  0.0 6       1.0 990     1.0 950     1.0 002    -2.0 330     1.0 993    -1.00 992
```

# SECTION 4

# NAUGATUCK RIVER CASE STUDY

## 4.1 BACKGROUND INFORMATION

The Naugatuck River is located in western Connecticut and has a long history of industrialization along its length. Hydropower generation was responsible for the initial development of the valley, with light metal production soon to follow. Three of the world's largest brass firms were located on its banks and, at the turn of the century, sixty percent of the world's brass products produced annually were manufactured in the valley. As a result of the light metal production industry, the electroplating industry emerged, and approximately 30,300 cubic meters/day of treated electroplating waste is currently being discharged into the Naugatuck River.

Most industrial discharges on the river currently adhere to Best Available Technology (BAT) guidelines. However, both long-term biological monitoring and recent toxicity testing have shown toxic impacts of metals. As a result, the Connecticut Department of Environmental Protection is presently developing allocation guidelines for the discharge of metals into the river. These guidelines will be based upon results of mathematical modeling being performed by the State Department of Environmental Protection. The data set available was to illustrate how to apply the model to field conditions and to calibrate MEXAMS to the Naugatuck River.

## 4.2 INPUT DESCRIPTION (MINTEQ)

This section will present information regarding the operation of the MINTEQ program. This discussion will include a description of the compartmentalized system used, and a line by line explanation of the computer inputs. The explanation will state any limitations, the variable names and their computer format code. Some of the EXAMS parameters were not used in this report due to the fact that the pollutants are priority metals, as opposed to synthetic organic chemical contaminants.

The MINTEQ program has a great deal of flexibility in the way the user defines the chemistry of the ecosystem being modeled. The program is capable of dealing with six different specie types, as described in the MINTEQ manual. The Type I specie is the component. The component is defined as the chemical specie chosen to represent each chemical constituent. Each component corresponds to a MINTEQ identification (ID) number. Table 4.1 provides a complete list of the components in MINTEQ. Type II complexes are defined as aqueous species which are combinations of two or more components. These complexes are not input by the user, but instead are output by the computer as a result of the Type I species input. Type III species are defined as a species with a fixed activity. Some examples of Type III species are components at fixed activity such as pH or pE, solid phases present in infinite supply, gases present at a fixed partial pressure, and redox reactions between two components. Type IV species are precipitated solids subject to complete dissolution. The Type III and Type IV solids are similar, except that Type IV solids have a finite mass. Type V species are dissolved solids subject to precipitation. These solid phases will only precipitate when the saturation index is exceeded. Finally, Type VI species are species not considered during equilibrium calculations. Instead, these species are considered after the equilibrium calculations are complete.

An example input file for the Naugatuck River is presented in Table 4.2, with the numbers on the left corresponding to line numbers, for explanation purposes. The first two lines are descriptive information for the sample site. The third line describes the water temperature (C), analytical units, and fixed ionic strength designation. If ionic strength is not to be fixed, 0.00 is input. Line four contains nine run specific user options: inorganic carbon input, debug print option, charge balance option, considered solids and print option, number of iterations, pH variation option, fixed ionic strength, numerical method selection, and output option. Refer to the user manual for a complete description of options.The fifth line contains adsorption paramaters. Line six through 24 are the component input lines, and the three fields correspond to the specie ID number, total analytical mass, and a guess for the log of the component activity. This section comprises the water quality data for a set of compartments in the ecosystem. The water quality data for the Naugatuck River was obtained from three sources (Medine and Conway, 1982, Curtis, 1982, and USGS, 1983). The water quality data used is presented in Table 4.3. Redox chemistry was not considered for several reasons - lack of data on redox active species and the generally oxic environment in the Naugatuck River.

TABLE 4.1 MINTEQ COMPONENTS

| Component | I.D. Number | Component | I.D. Number |
|---|---|---|---|
| E | 001 | $NH_4^+$ | 490 |
| $H_2O$ | 002 | $NO_2^-$ | 491 |
| $Ag^+$ | 020 | $NO_3^-$ | 492 |
| $Al^{3+}$ | 030 | $Na^+$ | 500 |
| $H_3AsO_3$ | 060 | $Ni^{2+}$ | 540 |
| $H_3AsO_4$ | 061 | $PO_4^{3-}$ | 580 |
| $H_3BO_3$ | 090 | $Pb^{2+}$ | 600 |
| $Ba^{2+}$ | 100 | $Rb^+$ | 680 |
| $Br^-$ | 130 | $HS^-$ | 730 |
| $CO_3^{2-}$ | 140 | S | 731 |
| Fulvate | 141 | $SO_4^{2-}$ | 732 |
| Humate | 142 | $H_4SiO_4$ | 770 |
| $Ca^{2+}$ | 150 | $Sr^{2+}$ | 800 |
| $Cd^{2+}$ | 160 | $U^{3+}$ | 890 |
| $Cl^-$ | 180 | $U^{4+}$ | 891 |
| $Cs^+$ | 220 | $UO_2^+$ | 892 |
| $Cu^{1+}$ | 230 | $UO_2^{2+}$ | 893 |
| $Cu^{2+}$ | 231 | | |
| $Fe^{2+}$ | 280 | | |
| $Fe^{3+}$ | 281 | | |
| $H^+$ | 330 | $Zn^{2+}$ | 950 |
| $I^-$ | 380 | SOH1 | 990 |
| $K^+$ | 410 | SOH2 | 991 |
| $Li^+$ | 440 | XPSIO | 992 |
| $Mg^{2+}$ | 460 | XPSIB | 993 |
| $Mn^{2+}$ | 470 | XPSID | 994 |
| $Mn^{3+}$ | 471 | SOHB | 995 |

(from Felmy et. al., 1983)

TABLE 4.2 MINTEQ INPUT

```
 1.  NAUGATUCK RIVER CONDITIONS (16-17 AUGUST 1983)
     COMPARTMENT 1 ZN-CU-PB ADSORPTION
 2.  KD MODEL: MATRIX OBTAINED FROM BEST AVAILABLE
     DATA PH=7.14
 3.  25.00 MG/L    0.00
 4.  0 0 1 0 0 0 0 0
 5.  1   0.00   0.00   0.00   0.00
 6.       150 2.000E+01  -3.80
 7.       460 3.500E+00  -3.90
 8.       500 1.890E+01  -2.50
 9.       140 3.422E+01  -5.50
10.       732 2.500E+01  -2.90
11.       180 3.800E+01  -2.80
12.       090 8.361E-02  -5.10
13.       410 3.090E+00  -4.25
14.       580 4.906E-01  -11.0
15.       770 8.320E+00  -6.50
16.       231 5.450E-02  -9.00
17.       950 1.750E-02  -8.00
18.       492 7.083E+00  -8.00
19.       470 3.550E-02  -7.00
20.       281 2.140E-01  -7.00
21.       600 6.000E-03  -8.00
22.       330 0.000E-00  -7.14
23.       991 0.000E-00   0.00
24.       990 0.000E+00   0.00
25.
26.    3   3
27.       330      7.14
28.       990
29.       991
30.
31.    2   3
32.  9909500 SOH-ZN                          -.24
33.        2    1.00 950    1.00 990
34.
35.  9916000 SOH-PB                          1.33
36.        2    1.00 600    1.00 991
37.
38.  9912310 SOH-CU                          0.20
39.        2    1.00 231    1.00 991
40.
41.
```

## TABLE 4.3 WATER QUALITY DATA

| Component | Concentration (mg/l) | Data Source |
|---|---|---|
| 150 - Ca | 1.50 E+01 | U.S.G.S. (1983) |
| 460 - Mg | 3.50 E+00 | U.S.G.S. (1983) |
| 500 - Na | 1.89 E+01 | Medine & Conway (1982) |
| 410 - K | 3.09 E+00 | Medine & Conway (1982) |
| 470 - Mn | * | Conn. - DEP (1982)** |
| 281 - Fe | * | Conn. - DEP (1982)** |
| 770 - SiO2 | 8.32 E+00 | U.S.G.S. (1983) |
| 950 - Zn | * | Conn. - DEP (1982)** |
| 090 - B | 8.36 E-02 | Medine & Conway (1982) |
| 231 - Cu | * | Conn. - DEP (1982)** |
| 732 - SiO4 | 2.50 E+01 | U.S.G.S. (1982) |
| 180 - Cl | 3.80 E+01 | U.S.G.S. (1982) |
| 140 - CO3 | 3.42 E+01 | Medine & Conway (1982) |
| 492 - NO3 | 7.08 E+00 | U.S.G.S. (1982) |
| 580 - PO4 | 4.91 E-01 | U.S.G.S. (1982) |
| 600 - Pb | * | Conn. - DEP** |
| 330 - H | * | Conn. - DEP** |

*These inputs are compartment dependent

**Connecticut State Department of Environmental Protection

The input for each component is the total analytical mass including the specification of total inorganic carbon as CO3.

The next line is blank, separating specie Type I from specie Type III. Line 26 corresponds to the specie type and the number of species of that type. The next three lines are for fixed pH and two surface sites for adsorption. After another blank line, the adsorption information is input. This input section consists of nine lines. The first line contains the type of modification and number of these modifications. Then each adsorption input has three corresponding lines of input. The first line is the adsorption description and the log Kd value for the reaction. Cu, Pb and Zn could have all been allowed to interact with either site 990 or 991. The differentiation between 990 and 991 was arbitrary and merely to illustrate the addition of two solids to the problem definition.

The adsorption routine chosen in this case was the "activity" Kd approach. The log Kd values were obtained by running the MINTEQ program without adsorption using the total dissolved metal as the input condition. By using the activity results and the field-observed particulate concentration for each metal in Equation 2.4, the "activity" Kd was obtained and log Kd was then input to the program. Table 4.4 presents the data obtained for each compartment, and the respective Kd values. The second line corresponds to the components and the stoichiometry of the reaction. Finally, the next two lines are blank to signify the end of the input file. Following the input of the MINTEQ data file, the next step is the creation of an EXAMS input file.

Organics were not included in the simulation because data were not available on dissolved organic carbon (DOC) or any of the individual organics comprising DOC. While including fulvates (component 141) or humates (component 142) may appear to be a way of improving the realism of the simulation, doing so with insufficient data concerning the complexation capacity of the DOC, particularly with respect to the fraction which could be broadly classified as humates or fulvates, could lead to equally unrealistic results. It is highly recommended that users of MINTEQ obtain DOC data whenever possible, and that organic complexation be included in the simulations to improve model realism.

## 4.3 INPUT DESCRIPTION (EXAMS)

The EXAMS input file is based on a compartmentalization of the riverine ecosystem. EXAMS is responsible for the metal transport and fate calculations. Figure 4.1 displays the initial compartmentalization scheme used for the Naugatuck

## TABLE 4.4 COMPARTMENT Kd DATA

| Compart- ment #-Type | Element | Free Ion Activity (M) | Particulate Conc. (M) | Log Kd |
|---|---|---|---|---|
| 1-E | Cu | 9.741 E-08 | 1.50 E-07 | .20 |
| | Pb | 9.940 E-10 | 2.17 E-08 | 1.33 |
| | Zn | 1.321 E-07 | 7.65 E-08 | -.24 |
| 2-B | Cu | 8.467 E-07 | 4.41 E-03 | 3.73 |
| | Pb | 9.300 E-07 | 2.79 E-03 | 3.48 |
| | Zn | 5.451 E-05 | 3.89 E-03 | 1.85 |
| 3-E | Cu | 1.634 E-07 | 1.34 E-07 | -.09 |
| | Pb | 2.551 E-09 | 2.17 E-08 | .93 |
| | Zn | 1.830 E-07 | 9.94 E-08 | -.26 |
| 4-B | Cu | 1.796 E-06 | 1.59 E-03 | 2.95 |
| | Pb | 1.834 E-06 | 3.00 E-04 | 2.21 |
| | Zn | 4.637 E-05 | 3.49 E-03 | 1.88 |
| 5-E | Cu | 4.422 E-08 | 3.93 E-08 | -.05 |
| | Pb | 2.234 E-09 | 2.17 E-08 | .99 |
| | Zn | 9.065 E-08 | 5.35 E-08 | -.23 |
| 6-B | Cu | 3.225 E-06 | 1.51 E-03 | 2.67 |
| | Pb | 2.543 E-06 | 3.07 E-04 | 2.08 |
| | Zn | 2.177 E-05 | 3.66 E-03 | 2.23 |

E - Epilimnion
B - Benthic

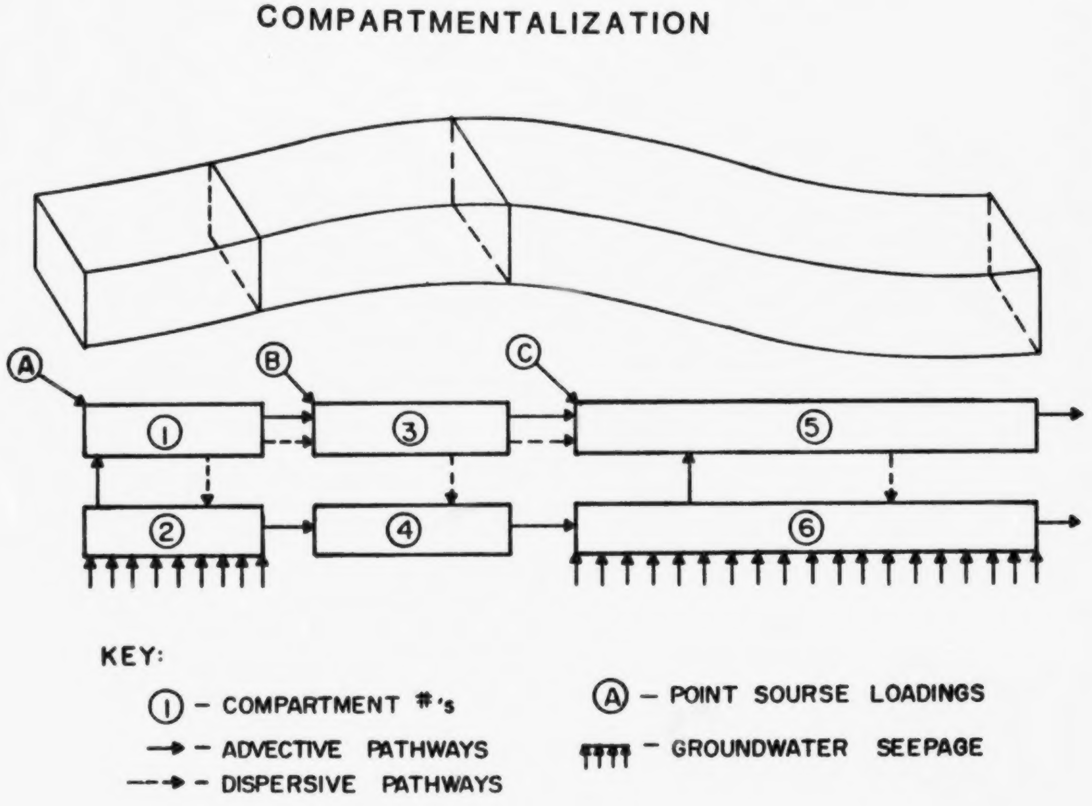

COMPARTMENTALIZATION
A
B
C
1
2
3
4
5
6
KEY:
1 - COMPARTMENT #'s
→ - ADVECTIVE PATHWAYS
--→ - DISPERSIVE PATHWAYS
A - POINT SOURSE LOADINGS
↑↑↑↑ - GROUNDWATER SEEPAGE

Figure 4.1 Initial Naugatuck River compartmentalization.

River system. Once the compartmentalization is selected, the EXAMS input file is generated. The file consists of 67 lines of input, reproduced in Table 4.5.

The first two lines contain three-letter abreviations for the chemical name and ecosystem name. The third line gives the number of chemical loadings. In this case, there are five loadings, and the next five lines specify each loading in Kg/hr for one of five types: point source, non-point source, rainfall, aerial drift and ground water seepage. The loadings are input from left to right for each compartment in the order previously stated. The next two lines are a description of the chemical, followed by a line of flags denoting which species of the organic toxicant can occur. In this case, zeros are input because the pollutant being investigated is a heavy metal. The next two lines are the ecosystem abreviation and description.

The ecosystem was divided into unequal compartment lengths representing well-defined segments based on actual point loadings. Compartments one and two are 1.3 miles long, compartments three and four are .3 miles long and compartments five and six are 6.7 miles long. Figure 4.2 displays the four different sample sites (East Albert St., Gulf Stream, Bogue Road, Bridge Abutment) within the stream segment selected for compartmentalization and modeling.

The next seven lines are the number of compartments, and the compartment code for each compartment. The compartments are classified as epilimnion (E), hypolimnion (H), littoral (L) or benthic (B). The compartment classification is then followed by the latitude input in degrees, and the wind velocity at 10 cm above the water surface (m/sec) for each compartment. Line 24 is the environmental volume (m3) for each compartment followed by entries of area (m2) and average depth (m) for each compartment.

The next section, lines 27 through 31, represent flows entering the ecosystem compartments. These flows are of the following type: stream flow (m3/hr), stream-born sediment load (Kg/hr), non-point source water flow (m3/hr), non-point source sediment loads (Kg/hr), and ground water seepage flow (m3/hr). The next input is average rainfall (mm/mo) in the geographic area, then the average cloudiness in tenths of full sky cover is input. From this point on in the data set, many parameters are input as zero because they deal with transformation of organic toxicants and not priority pollutant heavy metals.

The next six lines are inputs for average spectral irradiance immediately below the water surface. These inputs are not required for transformation of heavy metals. Line 40 corresponds to the evaporative water losses (mm/mo) from each

# TABLE 4.5 EXAMS INPUT

```
NAG
    5
    1 1.284E-02         0.         0.         0.         0.
    2        0.         0.         0.         0. 6.505E-04
    3 4.404E-03         0.         0.         0.         0.
    5 3.361E-02         0.         0.         0.         0.
    6        0.         0.         0.         0. 3.538E-04
HVM
Heavy Metal
0 0 0 0 0
NAG
NAUGATUCK RIVER CALIBRATION TEST RUN
    6
L
B
L
B
L
B
 41.80
 0.0000    0.0000     0.0000     0.0000     0.0000     0.0000
 9.316E+03 4.925E+02 3.353E+03 1.149E+02 7.903E+04 2.402E+03
 5.386E+04 5.366E+04 1.257E+04 1.257E+04 2.627E+05 2.627E+05
 0.17069  0.00914    0.17983    0.00914    0.3048     0.00914
 9.888E+020.000      4.694E+01 0.000      7.708E+02 0.000
 2.9668   0.000      0.489      0.000      5.528      0.000
 0.000    0.000      0.000      0.000      0.000      0.000
 0.000    0.000      0.000      0.000      0.000      0.000
 1.625E+02 1.626E-02 0.000      0.000      3.538E+02 3.538E-02
 00.00
 100.0
 0.000    0.000      0.000      0.000      0.000      0.000      0.000      0.000
 0.000    0.000      0.000      0.000      0.000      0.000      0.000      0.000
 0.000    0.000      0.000      0.000      0.000      0.000      0.000      0.000
 0.000    0.000      0.000      0.000      0.000      0.000      0.000      0.000
 0.000    0.000      0.000      0.000      0.000      0.000      0.000
     00.00      00.00      00.00      00.00      00.00      00.00
     00.00      00.00      00.00      00.00      00.00      00.00
 3.000    1.530      3.000      1.530      7.500      1.530
 0.000    115.2      0.000      115.2      0.000      115.2
    8
    1    3    5    2    4    4    6    2
    3    5    0    1    3    6    5    4
 1.000     1.000      1.000      0.900      0.900      0.100      1.000      0.100
    3
    1    3    5
    2    4    6
 5.386E+04 1.257E+04 2.627E+04
 8.992E-02 9.449E-02 1.570E-01
 5.000E-07 5.000E-07 5.000E-07
0.3800E-010.3800E-010.3800E-010.3800E-010.3800E-010.3800E-01
 25.00      25.00      25.00      25.00      25.00      25.00
 25.00      25.00      25.00      25.00      25.00      25.00
 23.50      23.50      23.50      23.50      23.50      23.50
 7.143      7.143      7.007      7.007      7.078      7.078
 6.857      6.857      6.993      6.993      6.922      6.922
0.1000E-08           0.00.1000E-080.5000E-09           0.00.1000E-08
 00.00      00.00      00.00      00.00      00.00      00.00
 00.00      00.00      00.00      00.00      00.00      00.00
 23.50      23.50      23.50      23.50      23.50      23.50
 00.00      00.00      00.00      00.00      00.00      00.00
 00.00      00.00      00.00      00.00      00.00      00.00
 00.00      00.00      00.00      00.00      00.00      00.00
 00.00      00.00      00.00      00.00      00.00      00.00
 00.00      00.00      00.00      00.00      00.00      00.00
 00.00      00.00      00.00      00.00      00.00      00.00
```

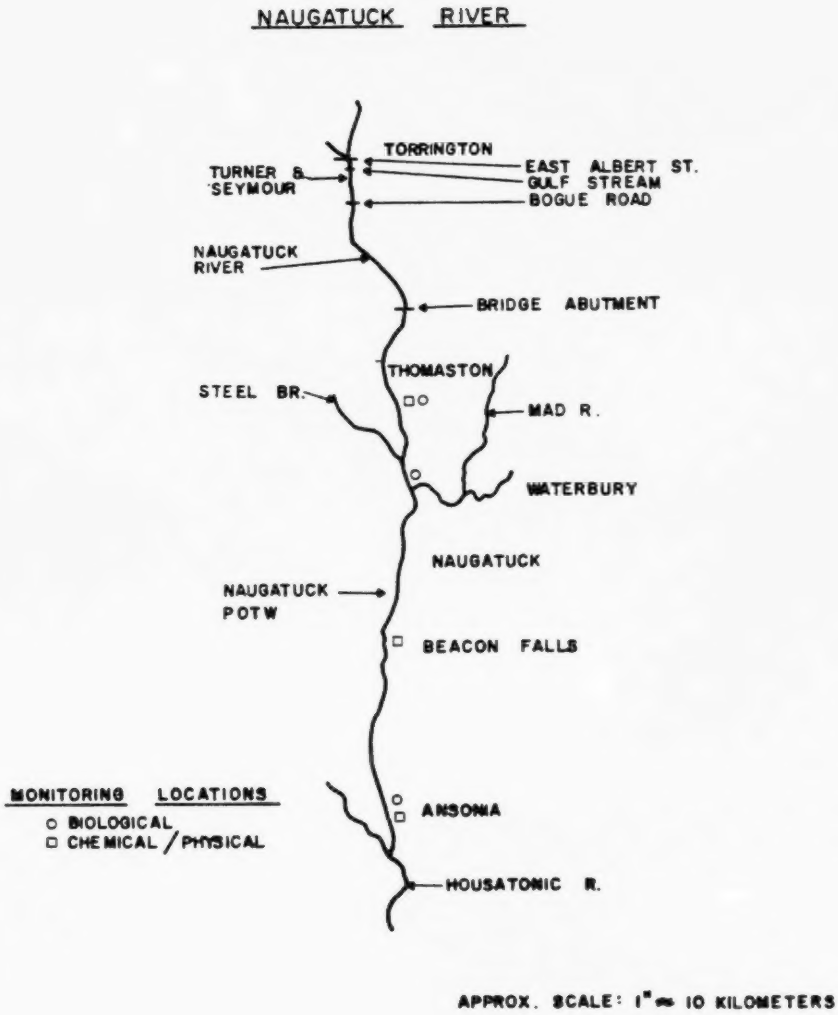

NAUGATUCK RIVER
TORRINGTON
TURNER & SEYMOUR
EAST ALBERT ST.
GULF STREAM
BOGUE ROAD
NAUGATUCK RIVER
BRIDGE ABUTMENT
THOMASTON
STEEL BR.
□○
MAD R.
○
WATERBURY
NAUGATUCK
NAUGATUCK POTW
□
BEACON FALLS
MONITORING LOCATIONS
○ BIOLOGICAL
□ CHEMICAL / PHYSICAL
○
□
ANSONIA
HOUSATONIC R.
APPROX. SCALE: 1" ≈ 10 KILOMETERS

Figure 4.2 Naugatuck River study location.

compartment. The next line is where suspended sediment concentrations (mg/l) are input if dealing with water column compartments and bulk density (g/cc) for benthic compartments. These inputs are followed by percent water in bottom sediments of benthic compartments. Water column compartments have inputs of zero for this variable.

The transport mechanisms of advection and dispersion are input in lines 43 - 52. Advection is input first, with the first line corresponding to the number of advective pathways. The next three lines are the source compartment, the receiving compartment and the proportion of the advective flow. The dispersive pathways are then input. The first line equates to the number of dispersive pathways. The source compartments are then entered followed by the receiving compartment and the description of the exchange pathway. The cross-sectional area (m2), characteristic length (m) and eddy dispersion coefficients (m3/hr) are the parameters required to describe the dispersive pathway. The characteristic length is defined as the distance from compartment center to compartment center.

The next three lines correspond to the organic carbon content of compartment sediment, cation and anion exchange capacity of the sediments. Line 56 is the average temperature for each compartment. The pH and pOH of each compartment are the next two inputs. Finally, the remaining lines are not required for the modeling of the Naugatuck riverine ecosystem for the migration and fate of priority pollutant metals.

For each compartment there is a corresponding MINTEQ input file, and it should be re-emphasized that each compartment is assumed to be completely mixed after the priority pollutant enters the compartment. After input files have been created for each compartment (MINTEQ), and the transformation and transport model (EXAMS) input file is complete, the MISP input file is created.

This file encompasses twenty-five lines in this example. These lines allow the interaction of MINTEQ with EXAMS and produce the MEXAMS system model. The first line corresponds to the selection of the computer mode (MINTEQ only, or coupled version). The metal selection is made next from the list of metals (As, Cd, Cu, Pb, Ni, Ag and Zn) and corresponding identification numbers in the MINTEQ components list. The next line corresponds to how many MINTEQ files are needed. The number of required files is dependent on the water quality data for the aquatic system. If the water quality data does not change significantly for each compartment, then one file is sufficient. Water quality fluctuations could be a result of wastewater treatment plant discharges, industrial discharges, overland runoff, etc.

The next group of lines corresponds to the number of compartments that match up with each MINTEQ file, followed by the compartment number that corresponds to each MINTEQ file. The next input is the number of times the programmer wants the steady state metal concentration updated. EXAMS initially assumes all metal is in the dissolved form, and by providing MINTEQ with these results, the actual dissolved, sediment sorbed, biosorbed and precipitated metal concentrations are obtained. EXAMS uses these updated calculations in the next simulation for fate and transport of the pollutant. Line seventeen relates to how often MINTEQ is used for persistence calculations. After steady state has been achieved, the pollutant loading is ceased and persistence calculations begin. These calculations are based on two system half-lives, which are divided into twelve equal time increments. This input will continue metal fraction updating throughout the persistence calculations. The next three inputs correspond to the output option, the MINTEQ file names for each compartment, and the EXAMS input file name. There are three output options available: the full MINTEQ output, aqueous species distribution, and all mass totals. This concludes the MISP input file. Table 4.6 is a sample of the MISP file.

## 4.4 OUTPUT (MINTEQ)

The MINTEQ output data received when the uncoupled mode is operated can be divided into seven sections. The first section is a duplication of the first five lines of the input file. Section two corresponds to the initial charge balance of the solution being modeled, prior to aqueous speciation. A large percent difference can be indicative that one or more major cations or anions may have been neglected when preparing the water quality input file. However, the water analysis may be entirely correct with the final speciation indicating an acceptable charge balance. Therefore, initial charge imbalance should be evaluated on a case by case basis (section 2 is presented in Table 4.7).

The third section provides an iterative output displaying the convergence of the first component in the input file to its actual speciated activity (Table 4.7). Also included in this section is the calculated molality, activity, Log activity, activity coefficient, and new Log K for all input components. The new Log K is the effective equilibrium constant after temperature and ionic strength corrections. This section can be used to enable the user to make a better guess for the activity in the input file.

The fourth section provides the output data for the six different specie types. The output for Type I components and

TABLE 4.6  MISP INPUT

```
3
231
6
1
1
1
2
1
3
1
4
1
5
1
6
3
4
3
NAUG1.DAT
NAUG2.DAT
NAUG3.DAT
NAUG4.DAT
NAUG5.DAT
NAUG6.DAT
EXAMS21.DAT
```

## TABLE 4.7 MINTEQ OUTPUT

```
CHARGE BALANCE: UNSPECIATED
     SUM OF CATIONS= 2.203E-03 SUM OF ANIONS = 2.863E-03
     PERCENT DIFFERENCE =    -13.04    (CATIONS - ANIONS)/(ANIONS + CATIONS)



          ITERATIONS DURING SOLVE
          ITER        NAME           TOTAL MOL     DIFF FXN      LOG ACTVTY
            1    CA                  4.991E-04   -2.910E-04     -3.80000
            2    CA                  4.991E-04   -6.766E-05     -3.38469
            3    CA                  4.991E-04    1.439E-04     -3.32420
            4    CA                  4.991E-04    2.858E-04     -3.43010
            5    CA                  4.991F-04   -1.933E-04     -3.62025
            6    CA                  4.991E-04    3.429E-06     -3.41555



OUTPUT DATA:   ITERATIONS =    6
 ID        NAME          ANAL MOL    CALC MOL   ACTIVITY     LOG ACTVTY     GAMMA     NEW LOGK     DIFF FXN
  150  CA               4.991E-04  4.815E-04 3.817E-04    -3.41830     .792686      .1009  -3.620E-07
  460  MG               1.440E-04  1.393E-04 1.107E-04    -3.95593     .794378      .1000  -1.034E-07
  500  NA               8.222E-04  8.211E-04 7.734E-04    -3.11159     .941939      .0260  -1.644E-07
  140  CO3              5.703E-04  3.792E-07 2.996E-07    -6.52348     .789951      .1024  -9.605E-08
```

Type II complexes are similar with the following headings: calculated molality, activity, Log activity, activity coefficient (GAMMA), new Log K, and the enthalpy of the reaction (DH). Type III fixed solids are of four basic categories, redox reactions, components at fixed activity, solid phases and gases at a fixed partial pressure. The output for these type species consists of calculated molality, Log molality, new Log K and the DH. In our case the Type III species fall into the category of fixed activities, thus any intuitive information from this section cannot be obtained. However, if solid phases were being dealt with, a positive calculated molality would equal the mass of solid precipitated. On the other hand, a negative calculated molality would equal the dissolved mass or mass added to the solution. No Type IV or Type V species were permitted from the list of solids which were supersaturated as indicated by MINTEQ. Chemical precipitation of heavy metals (Pb, Zn, Cu) has not been observed in the Naugatuck River although it cannot be precluded. The only significant, supersaturated solid phase predicted by MINTEQ which should be considered for inclusion in the simulation was ferric hydroxide NBS (specie 2028119). While allowing this solid to precipitate would be realistic, it's precipitation (approximately 3.8E-06 M) did not affect the behavior of Cu, Pb or Zn. In systems where much greater masses precipitate, this phenomenon would need to be included in describing the behavior of heavy metals due to co-precipitation or adsorption. In the Naugatuck River case, the precipitation of iron is a relatively minor force in regulating aqueous heavy metal concentration. Type V calculated molality would correspond to saturation index values. Type VI has two different interpretations for the calculated molality. If solid phase, it corresponds to saturation index. If aqueous species, it corresponds to activity of species. A sample of section four output is displayed in Table 4.8.

Section five presents the percentage distribution of Type I components and Table 4.9 is an example. The sixth section presents the amount of each Type I component in solution (aqueous mass), sorbed (sorbed mass) and precipitated (precipitated mass). The final charge balance is also presented, and if the final percent difference after aqueous speciation is less than five percent, the run is acceptable. A sample of section six output is presented in Table 4.9. The heavy metal under investigation in this case study is copper, and from Table 4.9 it can be seen that 14.3 percent of the copper is in the free ion form, 16.9 percent bound to surface sites with the remainder as inorganic complexes.

The final section provides the saturation indices for all minerals and solids in the data base. This section is used to determine if the saturation index of a particular mineral or

## TABLE 4.8 MINTEQ OUTPUT

```
  SPECIES:    TYPE  I - COMPONENTS
 ID         NAME          CALC MOL   ACTIVITY   LOG ACTVTY      GAMMA     NEW LOGK        DH
  150   CA                4.815E-04  3.817E-04    -3.41830     .792686        .101          0
  460   MG                1.393E-04  1.107E-04    -3.95593     .794378        .100          0
  800   NA                8.211E-04  7.734E-04    -3.11159     .941939        .026          0
  140   CO3               3.792E-07  2.996E-07    -6.52348     .789951        .102          0
  732   SO4               2.408E-04  1.891E-04    -3.72333     .785348        .105          0
  180   CL                1.072E-03  1.008E-03    -2.99650     .940572        .027          0
   90   H3BO3             1.341E-06  1.342E-06    -5.87224    1.000697       -.000          0
  410   K                 7.892E-05  7.423E-05    -4.12945     .940572        .027          0
  580   PO4               1.940E-11  1.137E-11   -10.94412     .586236        .232          0
  770   H4SIO4            8.643E-05  8.649E-05    -4.06305    1.000697       -.000          0
  231   CU+2              1.223E-07  9.686E-08    -7.01385     .791776        .101          0
  950   ZN                1.671E-07  1.323E-07    -6.87842     .791776        .101          0
  492   NO3               1.142E-04  1.074E-04    -3.96888     .940473        .027          0
  470   MN+2              6.220E-07  4.925E-07    -6.30758     .791776        .101          0
  281   FE+3              1.245E-14  7.545E-15   -14.12233     .606033        .218          0
  600   PB                1.286E-09  1.010E-09    -8.99549     .785813        .105          0

  SPECIES:    TYPE  II - COMPLEXES
 ID         NAME          CALC MOL   ACTIVITY   LOG ACTVTY      GAMMA     NEW LOGK        DH
1503300   CAOH +          1.409E-09  1.329E-09    -8.87633     .943302     -12.573     14.535
1501400   CAHCO3 +        1.944E-06  1.834E-06    -5.73669     .943302      11.370      1.790
1501401   CACO3 AQ        1.624E-07  1.625E-07    -6.78917    1.000697       3.152      4.030
1507320   CASO4 AQ        1.469E-05  1.470E-05    -4.83263    1.000697       2.309      1.470
1505800   CAHPO4 AQ       3.822E-07  3.825E-07    -6.41742    1.000697      15.085      -.230
1505801   CAPO4 -         1.325E-08  1.249E-08    -7.90342     .942758       6.485      3.100
1505802   CAH2PO4 +       2.204E-08  2.078E-08    -7.68242     .942758      20.986     -1.120
5001400   NACO3 -         4.555E-09  4.295E-09    -8.36707     .942758       1.294      8.911
5001401   NAHCO3 AQ       2.017E-07  2.018E-07    -6.69507    1.000697      10.080          0
6001800   PBCL +          4.307E-11  4.055E-11   -10.39199     .941520       1.626      4.380
6001801   PBCL2 AQ        6.475E-14  6.479E-14   -13.18849    1.000697       1.800      1.080
6001802   PBCL3 -         5.498E-17  5.176E-17   -16.28599     .941520       1.725      2.170
6001803   PBCL4 -2        3.186E-20  2.503E-20   -19.60149     .785813       1.485      3.530
6001400   PB(CO3)2-2      5.006E-12  3.959E-12   -11.40245     .785813      10.745          0
6003300   PBOH +          2.886E-10  2.719E-10    -9.56552     .941520      -7.684          0
6003301   PB(OH)2 AQ      1.459E-12  1.460E-12   -11.83554    1.000697     -17.120          0
6003302   PB(OH)3 -       2.458E-16  2.314E-16   -15.63557     .941520     -28.034          0
6003303   PB2OH +3        1.058E-17  6.152E-18   -17.21101     .581390      -6.124          0
6004920   PBNO3 +         1.705E-12  1.606E-12   -11.79437     .941520       1.196          0
6007320   PBSO4 AQ        1.074E-10  1.074E-10    -9.96882    1.000697       2.750          0
6003304   PB3(OH)4+2      6.282E-23  4.937E-23   -22.30658     .785813     -23.775     26.500
6001401   PBCO3 AQ        5.257E-09  5.261E-09    -8.27897    1.000697       7.240          0
6003305   PB(OH)4 -2      9.334E-21  7.335E-21   -20.13460     .785813     -39.594          0
6007321   PB(SO4)2-2      1.357E-13  1.066E-13   -12.97214     .785813       3.575          0
   SPECIES:    TYPE  III - FIXED SOLIDS
  ID          NAME          CALC MOL      LOG MOL    NEW LOGK       DH
     2   H2O              -9.247E-06      -5.034        .000          0
   991   SOH2             -1.751E-07      -6.757           0          0
   990   SOH1             -7.613E-08      -7.118           0          0
   330   H                -6.425E-04      -3.192       7.140          0

   SPECIES:    TYPE  VI - SPECIES NOT CONSIDERED
  ID          NAME          CALC MOL      LOG MOL    NEW LOGK       DH
3301403   CO2(GAS)         2.273E-03      -2.643      18.160       -.530
```

Reproduced from
best available copy.

# TABLE 4.9 MINTEQ OUTPUT

```
  PERCENTAGE DISTRIBUTION OF COMPONENTS

 CA
            96.5     PERCENT BOUND IN SPECIES     150   CA
             2.9     PERCENT BOUND IN SPECIES 1507320   CASO4 AQ

 CU+2
            14.3     PERCENT BOUND IN SPECIES     231   CU+2
            17.9     PERCENT BOUND IN SPECIES 9912310   SOH-CU
            18.2     PERCENT BOUND IN SPECIES 2311400   CUCO3 AQ
             1.7     PERCENT BOUND IN SPECIES 2313300   CUOH +
            44.9     PERCENT BOUND IN SPECIES 2313301   CU(OH)2 AQ
             2.6     PERCENT BOUND IN SPECIES 2311402   CUHCO3 +

 ZN
            62.4     PERCENT BOUND IN SPECIES     950   ZN
             2.2     PERCENT BOUND IN SPECIES 9507320   ZNSO4 AQ
             2.9     PERCENT BOUND IN SPECIES 9501400   ZNHCO3 +
             3.0     PERCENT BOUND IN SPECIES 9501401   ZNCO3 AQ
            28.4     PERCENT BOUND IN SPECIES 9909500   SOH-ZN


IDX        NAME        AQUEOUS MASS  SORBED MASS      PRECIPITATED MASS
  150  CA                4.987E-04          0                  0
  460  MG                1.430E-04          0                  0
  500  NA                9.221E-04          0                  0
  140  CO3               5.702E-04          0                  0
  732  SO4               2.601E-04          0                  0
  180  CL                1.072E-03          0                  0
   90  H3BO3             1.352E-06          0                  0
  410  K                 7.302E-05          0                  0
  580  PO4               5.164E-06          0                  0
  770  H4SIO4            8.656E-05          0                  0
  231  CU+2              7.042E-07      1.535E-07              0
  950  ZN                1.915E-07      7.613E-08              0
  492  NO3               1.142E-04          0                  0
  470  MN+2              6.438E-07          0                  0
  281  FE+3              3.832E-06          0                  0
  600  PB                7.360E-09      2.160E-08              0
    2  H2O               9.247E-06          0                  0
  330  H                 6.425E-04          0                  0
 CHARGE BALANCE: SPECIATED
       SUM OF CATIONS =  2.149E-03 SUM OF ANIONS   2.168E-03
       PERCENT DIFFERENCE =      -.43   (CATIONS - ANIONS)/(ANIONS + CATIONS)
 NONCARBONATE ALKALINITY =       0
 IONIC STRENGTH =    3.026E-03
```

solid has been exceeded. A positive Log SI means the solid is oversaturated. This also tells you that this solid could precipitate, and thus, if your environment favors this solid, the solid could be input as a Type V solid and allowed to precipitate. Finally, a line will be printed "NORMAL TERMINATION OF MINTEQ" and the output is complete. The final section is presented in Table 4.10.

## 4.5 OUTPUT (EXAMS)

The EXAMS output obtained when the coupled mode is selected is dependent upon the MISP file configuration. The parameter which controls the EXAMS output is the number of times EXAMS uses MINTEQ to update steady state metal concentrations. EXAMS utilizes MINTEQ three times to update steady-state metal concentrations in the Naugatuck River test case. The selection of this parameter is based on trial and error; the programmer examines the output obtained while varying the input and determines when system steady state is achieved. System steady state is defined as an equilibrium between the partioning achieved with EXAMS and MINTEQ.

The EXAMS output file received after each steady state calculation will be divided into three sections. The first section consists of 13 tables, which were obtained from the initial EXAMS calculation. The initial EXAMS calculation assumes the pollutant is in the aqueous form. Tables 2 - 8 (all shown in Table 4.11) are echoes of the EXAMS input data. Table 1 is not printed because the pollutant in question is a heavy metal and not an organic. If the pollutant had been an organic, Table 1 would have been an echo of the organic input data.

The next section includes Tables 9 - 14 (all shown in Table 4.12). These five tables are the transport profile, the kinetic profile, the canonical profile, toxicant loadings by system element, the distribution of the chemical at steady state (the water column and sediments), the average, maximum and minimum concentrations at steady state. Table 10, the kinetic profile is for organic toxicants only. These five tables are repeated the number of times EXAMS uses MINTEQ to update steady state metal concentrations. For the Naugatuck River test case, this occurred three times. The most important of the three outputs is the last repetition, because it is the output obtained when system steady state has been achieved for the water column and sediments.

The third section of output is encompassed in Table 15 - 17, the analysis of steady state fate, the simulation of system response after load ceases, and the exposure analysis summary.

TABLE 4.10  MINTEQ OUTPUT

```
SATURATION INDICES FOR ALL MINERALS AND SOLIDS
   ID        NAME           LOG SI      LOG K    MIN LOGK    MAX LOGK    LOG IAP        DH
 6015000 ANHYDRITE          -2.505      4.637           0           0     -7.142      3.769
 5015000 ARAGONITE          -1.606      8.336           0           0     -9.942      2.615
 5046000 ARTINITE           -9.755     -9.600           0           0      -.155     28.742
 2046000 BRUCITE            -6.463    -16.792           0           0     10.324     25.840
 5015001 CALCITE            -1.467      8.475       8.560           0     -9.942      2.585
 2077000 CHALCEDONY          -.540      3.523           0           0     -4.063     -4.615
 8646000 CHRYSOTILE         -9.342    -32.188           0           0     22.846     52.485
 8246000 CLINOENSTITE       -5.077    -11.338     -10.972     -11.632      6.261     20.015
 2077001 CRISTOBALITE        -.476      3.587           0           0     -4.063     -5.500
 8215000 DIOPSIDE           -6.826    -19.886           0           0     13.060     32.280
 5015002 DOLOMITE           -3.421     17.000           0           0    -20.421      8.290
 6046000 EPSOMITE           -5.539      2.140           0           0     -7.679     -2.820
 8646003 SEPIOLITE(C)       -7.454    -15.913           0           0      8.459     27.268
 2028100 FERRIHYDRITE        2.407     -4.891      -1.557      -4.996      7.298          0
 4128100 FEOH)2.7CL.3        7.297      3.040           0           0      4.257          0
 6028100 FE2(SO4)3         -42.995     -3.580        .650           0    -39.415     59.120
 8046000 FORSTERITE        -11.713    -28.298           0           0     16.585     48.510
 2028102 GOETHITE            6.798      -.500           0           0      7.298     14.480
 6015001 GYPSUM             -2.294      4.848           0           0     -7.142      -.261
 4150000 HALITE             -7.690     -1.582           0           0     -6.108      -.918
 3028100 HEMATITE           18.603      4.008           0           0     14.595     30.845
 5015003 HUNTITE           -11.412     29.968           0           0    -41.380     25.760
 5046001 HYDRMAGNESIT      -22.828      8.766           0           0    -31.594     52.210
 6050000 JAROSITE NA         1.115     11.200           0           0    -10.085     36.180
 8215002 WOLLASTONITE       -6.197    -12.996           0           0      6.799     19.498
 8215003 P-WOLLSTANIT       -7.047    -13.846           0           0      6.799     21.068
 8015001 CA-OLIVINE        -19.989    -37.649           0           0     17.660     54.695
 8015002 LARNITE           -21.481    -39.141           0           0     17.660     57.238
 6015007 CA3SIO5           -45.345    -73.867           0           0     28.522    106.335
 8015003 MONTICELLITE      -13.149    -30.272           0           0     17.123     49.421
 8015005 AKERMINITE        -23.551    -47.472           0           0     23.921     76.445
 8015004 MERWINITE         -33.760    -68.543           0           0     34.783    107.111
 3028102 LEPIDOCROCIT        5.927     -1.371           0           0      7.298          0
                      NORMAL TERMINATION OF MINTEQ
```

TABLE 4.11 EXAMS OUTPUT

```
ECOSYSTEM: NAUGATUCK RIVER CALIBRATION TEST RUN
----------------------------------------------------------------------------
TABLE 2.  INPUT DATA DESCRIBING ENVIRONMENT: GLOBAL PARAMETERS.
----------------------------------------------------------------------------
KOUNT= 10     RAIN(MM/MO)=   .0        CLOUD(10THS)=  1.0E+02 LAT= 41.80
IRRADIANCE (WLAM,P/SQ CM/SEC/N NM):    .0          .0          .0
  .0          .0          .0          .0          .0          .0
  .0          .0          .0          .0          .0          .0
  .0          .0          .0          .0          .0          .0
  .0          .0          .0          .0          .0          .0
  .0          .0          .0          .0          .0          .0
  .0          .0          .0          .0          .0          .0
----------------------------------------------------------------------------
```

(continued)

TABLE 4.11 (continued)

```
------------------------------------------------------------------------
TABLE 3.  INPUT DATA DESCRIBING ENVIRONMENT: BIOLOGICAL PARAMETERS.
------------------------------------------------------------------------
 # TY   BIOMS       PLRA       BIOTM       BACTO      ACBAC       CHL
         (1)         (2)       DEG C.       (3)        (2)        MG/L
------------------------------------------------------------------------
  1L    .0          .0         23.50       .0         .0         .0
  2B    .0          .0         23.50       .0         .0
  3L    .0          .0         23.50       .0         .0         .0
  4B    .0          .0         23.50       .0         .0
  5L    .0          .0         23.50       .0         .0         .0
  6B    .0          .0         23.50       .0         .0
  7L    .0          .0         23.50       .0         .0         .0
  8B    .0          .0         23.50       .0         .0
  9L    .0          .0         23.50       .0         .0         .0
 10B    .0          .0         23.50       .0         .0
------------------------------------------------------------------------
 (1) UNITS: MG/L IN WATER COLUMN (L,H,B); G (D.W.)/SQUARE METER IN (B).
 (2) DIMENSIONLESS NUMBERS.
 (3) UNITS: CELLS/ML IN L, E, H; CELLS/100 G D.W. IN B.
```

(continued)

TABLE 4.11 (continued)

```
-------------------------------------
TABLE 4.  INPUT DATA DESCRIBING ENVIRONMENT: DEPTHS AND INFLOWS.
-------------------------------------------------------------------------
 # TY   DEPTH       STFLO      STSED      NPSFL      NPSED      INTFL
          M       CU M/HR     KG/HR     CU M/HR     KG/HR     CU M/HR
-------------------------------------------------------------------------
  1L   .1707       988.8      2.967                            162.5
  2B   9.140E-03                                               1.626E-02
  3L   .1798       46.94      .4890
  4B   9.140E-03
.3048    770.8       5.528                          117.9
  6B   9.140E-03                                               1.179E-02
  7L   .3048                                                   117.7
  8B   9.140E-03                                               .1179
  9L   .3048                                                   117.7
 10B   9.140E-03                                               .1533
```

(continued)

## TABLE 4.11 (continued)

```
--------------------------------------------------------------------------
TABLE 5.  INPUT DATA DESCRIBING ENVIRONMENT: SEDIMENT CHARACTERISTICS.
--------------------------------------------------------------------------
# TY   SDCHR        PCTWA        FROC         CEC         AEC        DOC
        (1)          (2)          (3)         (4)         (4)        MG/L
--------------------------------------------------------------------------
 1L    3.000                   3.800E-02   25.00       25.00        .0
 2B    1.530        115.2      3.800E-02   25.00       25.00
 3L    3.000                   3.800E-02   25.00       25.00        .0
 4B    1.530        115.2      3.800E-02   25.00       25.00
 5L    7.500                   3.800E-02   25.00       25.00        .0
 6B    1.530        115.2      3.800E-02   25.00       25.00
 7L    7.500                   3.800E-02   25.00       25.00        .0
 8B    1.530        115.2      3.800E-02   25.00       25.00
 9L    7.500                   3.800E-02   25.00       25.00        .0
10B    1.530        115.2      3.800E-02   25.00       25.00
--------------------------------------------------------------------------
 (1) UNITS: MG/L SUSPENDED SEDIMENT IN L, E, H; BULK DENSITY (G/CC) IN B
 (2) 100 * F.W./D.W. IN B.
 (3) DIMENSIONLESS.
 (4) MEQ/100 GRAMS DRY WEIGHT.
```

(continued)

TABLE 4.11 (continued)

```
TABLE 6.  INPUT DATA DESCRIBING ENVIRONMENT: AERATION, LIGHT, MISC.
--------------------------------------------------------------------------------
# TY    K02          WIND         CMPET       DFAC        EVAP          AREA
      CM/HR @20   M/S @10 CM      /M          M/M        MM/MON         SQ M
--------------------------------------------------------------------------------
  1L     .0           .0          1.161        .0          .0         5.386E+04
  2B                                                                  5.386E+04
  3L     .0           .0          1.161        .0          .0         1.257E+04
  4B                                                                  1.257E+04
  5L     .0           .0          2.691        .0          .0         8.757E+04
  6B                                                                  8.757E+04
  7L     .0           .0          2.691        .0          .0         8.757E+04
  8B                                                                  8.757E+04
  9L     .0           .0          2.691        .0          .0         8.757E+04
 10B                                                                  8.757E+04
```

(continued)

TABLE 4.11 (continued)

```
TABLE 7.  INPUT DATA DESCRIBING ENVIRONMENT: ADVECTIVE INTERCONNECTIONS.
-------------------------------------------------------------------------
COMP. NO. (JFRAD)      1          3          5          7          9
CONNECTED (ITOAD)      3          5          7          9          0
ADVECTION (ADVPR)   1.00       1.00       1.00       1.00       1.00
COMP. NO. (JFRAD)      2          4          6          8         10
CONNECTED (ITOAD)      1          3          5          7          9
ADVECTION (ADVPR)   .900       .900       .900       .240       .380
COMP. NO. (JFRAD)      2          4          6          8         10
CONNECTED (ITOAD)      4          6          8         10          0
ADVECTION (ADVPR)   .100       .100       .100       .760       .620

-------------------------------------------------------------------------
TABLE 8.  INPUT DATA DESCRIBING ENVIRONMENT: TURBULENT INTERCONNECTIONS.
0COMP. NO. (JTURB)        1           3           5           7           9
CONNECTED (ITURB)         2           4           6           8          10
X-SECTION (XSTUR)  5.39E+04    1.26E+04    8.76E+04    8.76E+04    8.76E+04
CHAR. LN. (CHARL)  8.99E-02    9.45E-02    .157        .157        .157
EDDY DISP. (DSP)   5.00E-07    5.00E-07    5.00E-07    5.00E-07    5.00E-07
```

TABLE 4.12 EXAMS OUTPUT

```
------------------------------------------------------------------------------
TABLE 9.  TRANSPORT PROFILE OF ECOSYSTEM.
------------------------------------------------------------------------------
CP T*   VOLUME     SEDIMENT   WATER FLOW  SED. FLOW  RESIDENCE TIME (DAYS)
   Y  (CUBIC M)  MASS (KG) (CU. M/DAY) (KG/DAY)     WATER     SEDIMENTS
------------------------------------------------------------------------------
  1L   9.32E+03   27.9        2.76E+04   313.        .337       8.93E-02
  2B   495.       6.58E+05    1.84       9.80E+03   54.3        67.1
  3L   3.35E+03   10.1        2.88E+04   114.        .117       8.85E-02
  4B   115.       1.53E+05    .361       2.15E+03   64.2        71.1
  5L   2.63E+04   198.        5.01E+04   471.        .526       .420
  6B   801.       1.06E+06    1.64       9.08E+03   98.7        117.
  7L   2.63E+04   198.        5.29E+04   2.69E+03    .498       7.34E-02
  8B   801.       1.06E+06    4.21       2.32E+04   38.4        45.9
  9L   2.63E+04   198.        5.57E+04   1.76E+03    .473       .112
 10B   801.       1.06E+06    7.20       3.28E+04   22.4        32.5
------------------------------------------------------------------------------
* COMP. TYPE: "L"=LITTORAL; "E"=(EPI) AND "H"=(HYPO)LIMNION; "B"=BENTHIC
```

(continued)

TABLE 4.12 (continued)

TABLE 10. KINETIC PROFILE OF ORGANIC TOXICANT. RATE CONSTANTS DERIVED FROM COUPLING OF TOXICANT CHARACTERISTICS TO ECOSYSTEM PROPERTIES.

| CP TY* | PSEUDO-FIRST-ORDER RATE CONSTANTS (/HR) HYDROLYSIS | PHOTOLYSIS | OXIDATION | BIOLYSIS | VOLATILITY | TRANSPORT |
|---|---|---|---|---|---|---|
| 1L | .0 | .0 | .0 | .0 | .0 | .197 |
| 2B | .0 | .0 | .0 | .0 | .0 | 6.21E-04 |
| 3L | .0 | .0 | .0 | .0 | .0 | .369 |
| 4B | .0 | .0 | .0 | .0 | .0 | 5.86E-04 |
| 5L | .0 | .0 | .0 | .0 | .0 | 8.56E-02 |
| 6B | .0 | .0 | .0 | .0 | .0 | 3.56E-04 |
| 7L | .0 | .0 | .0 | .0 | .0 | .146 |
| 8B | .0 | .0 | .0 | .0 | .0 | 9.08E-04 |
| 9L | .0 | .0 | .0 | .0 | .0 | .133 |
| 10B | .0 | .0 | .0 | .0 | .0 | 1.28E-03 |

* COMP. TYPE: "L"=LITTORAL; "E"=(EPI) AND "H"=(HYPO)LIMNION; "B"=BENTHIC

(continued)

TABLE 4.12  (continued)

```
TABLE 11.  CANONICAL PROFILE OF ECOSYSTEM.
-----------------------------------------------------------------------------------
CP T*  PH    POH   TEMP REAERATION COMPOSITE BACTERIAL  OXIDANT   DISSOLVED
   Y               DEG.   COEFF.   LIGHT AVE POP. SIZE   CONC.    PERCENT
   P                C.     M/HR        %     CELLS/**   (MOLAR)       %
-----------------------------------------------------------------------------------
  .0        .0          .0         1.00E-09  78.5
  2B  7.14  6.86 23.5    .0          .0         .0      .0        6.91E-03
  3L  7.01  6.99 23.5    .0          .0         .0      1.00E-09  89.8
  4B  7.01  6.99 23.5    .0          .0         .0      5.00E-10  3.11E-02
  5L  7.08  6.92 23.5    .0          .0         .0      .0        68.1
  6B  7.08  6.92 23.5    .0          .0         .0      1.00E-09  2.28E-02
  7L  7.08  6.92 23.5    .0          .0         .0      1.00E-09  87.2
  8B  7.08  6.92 23.5    .0          .0         .0      5.00E-10  3.01E-03
  9L  7.08  6.92 23.5    .0          .0         .0      1.00E-09  84.3
 10B  7.08  6.92 23.5    .0          .0         .0      .0        4.06E-03
-----------------------------------------------------------------------------------
* COMP. TYPE: "L"=LITTORAL; "E"=(EPI) AND "H"=(HYPO)LIMNION; "B"=BENTHIC
** ACTIVE BACTERIAL  POPULATIONS AS CELLS/ML IN WATER COLUMN,
   CELLS/100 G (DRY WEIGHT) OF SEDIMENTS IN BOTTOM SEDIMENTS.
```

(continued)

TABLE 4.12 (continued)

TABLE 12. TOXICANT LOADINGS (KG/HR) BY SYSTEM ELEMENT.

| ELEMENT | STREAM FLOW | RAINFALL | INTERFLOW | NPS LOAD | DRIFT LOAD |
|---|---|---|---|---|---|
| 1 | 1.284E-02 | | | | |
| 2 | | | 6.505E-04 | | |
| 3 | 4.404E-03 | | | | |
| 4 | | | | | |
| 5 | 3.361E-02 | | | | |
| 6 | | | 1.179E-04 | | |
| 7 | | | | | |
| 8 | | | 1.179E-04 | | |
| 9 | | | | | |
| 10 | | | 1.179E-04 | | |

(continued)

TABLE 4.12 (continued)

```
-----------------------------------------------------------------------------------------
TABLE 13. DISTRIBUTION OF CHEMICAL AT STEADY STATE: IN THE WATER COLUMN:
-----------------------------------------------------------------------------------------
COMP STEADY-STATE RESIDENT MASS       ********* TOXICANT CONCENTRATIONS *********
 #      2                            TOTAL   DISSOLVED SORBED BY SORBED BY PRECIP TO
                                                       BIOTA   SEDIMENTS SEDIMENTS
     G/M        KILOS         %        MG/*      MG/L      UG/G      MG/KG      MG/L
--- ------     ------      ------  --------- --------- --------- --------- ---------
  1 1.99E-03  .1073          6.87  1.15E-02  9.05E-03  .0        826.       .0
  3 3.98E-03  5.005E-02      3.20  1.49E-02  1.34E-02  .0        507.       .0
  5 7.43E-03  .6504         41.63  2.47E-02  1.68E-02  .0        1.05E+03   .0
  7 4.84E-03  .4235         27.10  1.61E-02  1.40E-02  .0        274.       .0
  9 3.78E-03  .3311         21.19  1.26E-02  1.06E-02  .0        263.       .0
 SUBTOTAL:    1.562          1.90
 AND IN THE BOTTOM SEDIMENTS:
  2 .256      13.79         17.13  21.0      9.53E-03  .0        21.0       .0
  4 .109      1.370          1.70  8.98      1.84E-02  .0        8.98       .0
  6 .137      12.03         14.94  11.3      1.70E-02  .0        11.3       .0
  8 .332      29.10         36.14  27.4      5.42E-03  .0        27.4       .0
 10 .277      24.23         30.10  22.8      6.09E-03  .0        22.8       .0
 SUBTOTAL:    80.53         98.10
TOTAL MASS (KILOGRAMS) =      82.09
```

(continued)

TABLE 4.12 (continued)

```
TABLE 14.  AVERAGE, MAXIMUM, AND MINIMUM CONCENTRATIONS AT STEADY STATE.
--------------------------------------------------------------------------------

 1
  CP)TOTAL      CP)DISSOLVED  CP)SEDIMENTS  CP)BIOTA      CP)PRECIP     CP)MASS


       MG/*          MG/L          MG/KG         UG/G          MG/L          G/M

   -----------   -----------   -----------   -----------   -----------   -----------


WATER COLUMN:
AV        1.60E-02      1.28E-02      584.              .0            .0       4.4E-03

MA   5)  2.47E-02  5)  1.68E-02  5)  1.05E+03  9)  .0       9)  .0      5)  7.4E-03

MI   1)  1.15E-02  1)  9.05E-03  9)  263.      9)  .0       9)  .0      1)  2.0E-03

BOTTOM SEDIMENTS:
AV        18.3          1.13E-02      18.3              .0            .0         .22

MA   8)  27.4      4)  1.84E-02  8)  27.4     10)  .0      10)  .0      8)  .33

MI   4)  8.98      8)  5.42E-03  4)  8.98     10)  .0      10)  .0      4)  .11
--------------------------------------------------------------------------------

1 NUMBER IN HALF-PARENS CP) INDICATES COMPARTMENT WHERE VALUE WAS FOUND.
* TOTAL CONCENTRATION AS MG/L IN WATER COLUMN, AS MG/KG IN SEDIMENTS.
```

(continued)

These three tables contain the persistence calculation performed by EXAMS. These tables are presented in Table 4.13. The final portion of the program output is the MISP output.

## 4.6 OUTPUT (MISP)

This section as previously stated provides a summary of the EXAMS-MINTEQ interactions. These interactions include steady state calculations made to achieve system steady state, and calculations made during the persistence to update metal fractions. For the Naugatuck River test case, steady state concentrations were updated three times to obtain system equilibrium, and updated again two times during the persistence calculation. This totals five interactions between EXAMS and MINTEQ, and the MISP output file is presented in Table 4.14.

## 4.7 SYSTEM COMPUTATIONAL REPRESENTATION AND CALIBRATION

### 4.7.1 Model Calibration - General

The main issue surrounding model calibration and verification is obtaining estimates for model parameters and comparing prediction of the output with the actual observed outputs. Ideally, several data sets are available for independent calibration and verification steps. In cases of limited data, split-data testing is often recommended (Donigian, 1982) to allow calibration with one portion of the data and verification with the remainder. Unfortunately, chemical fate data in many cases does not present this luxury. To divide an already limited data base further may lead to inadequate calibration and misleading verification results. In the case of the Naugatuck River data, limited data were available and permitted only the calibration of the model.

Subjective variation of parameter values (benthic Kd's, advective groundwater paths, dispersion coefficients, etc,) and a qualitative comparison of model solution and observation is the most common approach to model calibration (Chapra and Reckhow, 1983; Beck, 1983). Through this procedure, the calibration process attempts to "account for (1) spatial variations not represented by the model formulation; (2) functional dependencies of parameters that are either non-quantifiable, unknown and/or not included in the model algorithms; or (3) extrapolation of laboratory measurements of parameters to natural field conditions" (Donigian, 1982). During calibration, the analyst may choose to adjust some of

TABLE 4.13 EXAMS OUTPUT

```
CHEMICAL: Heavy Metal
ECOSYSTEM: NAUGATUCK RIVER CALIBRATION TEST RUN
------------------------------------------------------------------------
TABLE 15.  ANALYSIS OF STEADY-STATE FATE OF ORGANIC TOXICANT.
------------------------------------------------------------------------
             PROCESS                    MASS FLUX    % OF LOAD    HALF-LIFE*
                                         KG/DAY                       DAYS
      ------------------------          ---------    ---------    ---------
      HYDROLYSIS                         .0            0.0          ---
      OXIDATION                          .0            0.0          ---
      PHOTOLYSIS                         .0            0.0          ---
  ALL CHEMICAL PROCESSES                 .0            0.0          ---
------------------------------------------------------------------------
      WATER COLUMN (BACTERIA)            .0            0.0          ---
      BOTTOM SEDIMENTS (BACTERIA)        .0            0.0          ---
  TOTAL BIOLYSIS                         .0            0.0          ---
------------------------------------------------------------------------
      VOLATILIZATION                     .0            0.0          ---
      WATER-BORNE EXPORT                1.245        100.00        45.72
------------------------------------------------------------------------
TRANSFORMATION AND TRANSPORT            1.245        100.00
TOTAL SYSTEM LOAD                       1.245
RESIDUAL ACCUMULATION RATE:             1.341E-06      0.00
------------------------------------------------------------------------
* HALF-LIVES ARE ESTIMATES BASED ON A FIRST-ORDER RATE APPROXIMATION.
```

(continued)

TABLE 4.13 (continued)

```
CHEMICAL: Heavy Metal
ECOSYSTEM: NAUGATUCK RIVER CALIBRATION TEST RUN
-------------------------------------------------------------------------------
TABLE 16.  SIMULATION OF SYSTEM RESPONSE AFTER LOAD CEASES.
-------------------------------------------------------------------------------
TIME       AVERAGE POLLUTANT CONCENTRATIONS             MASS OF POLLUTANT
-----      --------------------------------             -----------------
DAYS     WATER COLUMN         BOTTOM SEDIMENTS        WATER COL    SEDIMENTS
      - ------------------   ---------------------   ---------    ---------
      FREE(MG/L) SED(MG/KG)  PORE(MG/L) SED(MG/KG)   TOTAL KG     TOTAL KG

  0.    1.28E-02    584.      1.13E-02    18.3        1.562        80.5
  8.    3.75E-03    165.      1.06E-02    17.0        .4264        74.5
 16.    3.46E-03    153.      9.91E-03    15.6        .3934        68.4
 24.    3.20E-03    142.      9.26E-03    14.4        .3630        62.7
```

(continued)

TABLE 4.13 (continued)

```
TABLE 17.  EXPOSURE ANALYSIS SUMMARY.
----------------------------------------------------------------------
EXPOSURE:
 A. MAXIMUM CONC. IN WATER COLUMN:  1.7E-02 MG/L DISSOLVED,  2.5E-02 TOT
    MAX. CONC. IN BOTTOM SEDIMENT:  1.8E-02 MG/L DISSOLVED IN PORE WATER
 B. BIOSORPTION - MAX. CONCENTRATION - PLANKTON:  .0      UG/G
                                       BENTHOS:   .0      UG/G
 C. MAXIMUM TOT. CONC. IN SEDIMENT DEPOSITS:  27.     MG/KG (DRY WEIGHT)
FATE:
 A. TOTAL STEADY-STATE ACCUMULATION:  82.     KG;  1.90% IN WATER COL.,
       98.10% IN BOTTOM SEDIMENTS.
 B. TOTAL LOAD:  1.2     KG/DAY - DISPOSITION:   0.0 % VIA CHEMICAL
      TRANSFORMATIONS,   0.0 % BIOTRANSFORMED,   0.0 % VOLATILIZED,
      100.00% EXPORTED VIA OTHER PATHWAYS.
PERSISTENCE:
 A. AT THE END OF A  96.0     DAY RECOVERY PERIOD, THE WATER COLUMN HAD
      LOST  76.77% OF ITS INITIAL TOXICANT BURDEN; THE SEDIMENTS HAD
      LOST  22.16% OF THEIR INITIAL BURDEN (  23.20% REMOVAL OVERALL).
 B. SYSTEM SELF-PURIFICATION TIME IS ROUGHLY******* YEARS.
  32.    2.96E-03   131.        8.67E-03   13.2        .3352        57.4
  40.    2.74E-03   122.        8.10E-03   12.2        .3094        52.6
  48.    2.53E-03   113.        7.57E-03   11.2        .2857        48.2
  56.    2.34E-03   105.        7.07E-03   10.3        .2638        44.2
  64.    2.16E-03   97.1        6.60E-03   9.46        .2436        40.5
  72.    2.00E-03   90.0        6.17E-03   8.71        .2252        37.2
  80.    1.85E-03   83.5        5.76E-03   8.02        .2082        34.1
  88.    1.71E-03   77.5        5.38E-03   7.39        .1926        31.3
```

TABLE 4.14 MISP OUTPUT

```
UPDATED CONCENTRATIONS FROM MINTEQ (MG/L)
UPDATED CONCENTRATIONS FROM MINTEQ (MG/L)
COMPARTMENT      AQUEOUS     ADSORBED     PRECIPITATED
COMPARTMENT      AQUEOUS     ADSORBED     PRECIPITATED
       1      9.024E-03   2.478E-03    0.0
       2      9.532E-03   1.379E+02    0.0
       3      1.341E-02   1.519E-03    0.0
       4      1.836E-02   5.897E+01    0.0
       5      1.684E-02   7.880E-03    0.0
       6      1.697E-02   7.435E+01    0.0
       7      1.404E-02   2.065E-03    0.0
       8      5.420E-03   1.798E+02    0.0
       9      1.061E-02   1.970E-03    0.0
      10      6.094E-03   1.500E+02    0.0
CONCENTRATIONS COMPUTED BY EXAMS IN MG/L
CONCENTRATIONS COMPUTED BY EXAMS IN MG/L
```

the parameters to improve model predictions or to alter the structure of the relationships (or system physical representation) between the variables in the model.

During calibration of the Naugatuck River data set, it was necessary to modify the configuration (from a six to a ten compartment representation) and then proceed to adjust parameters to achieve the desired degree of comparability. For this tutorial, the demonstration of both procedures is instructive to future model users.

It is recommended that future users of the model consider the data requirements for both calibration and verification stages in model usage and establish more formal methods for parameter estimation and error determinations as described in Chapra and Reckhow (1983), Beck (1983), and Donigian, (1982) and others. It should be noted that, since the Naugatuck River test case represents a calibration of MEXAMS only, there is incomplete confidence that the model will perform as desired.

### 4.7.2 System Configuration

The first step in the calibration was to determine which model inputs have the least reliability. These are the parameters that will be adjusted to perform a sensitivity analysis. Any sensitivity analysis is system dependent because certain input parameters may be more or less sensitive depending on the system being modeled. The first decision to be made in the utilization of MEXAMS was to select a system configuration. There are many possible configurations due to the possible advective and dispersive pathways. The two initial configurations chosen for this test case are presented in Figure 4.3. The main difference between configuration one and configuration two is the advective pathways. Configuration one allows flow to exit the system through the sediments via compartment six and has no advective flow through compartment four, configuration two is just the opposite. Originally, both of these configurations had the entire groundflow routed through the benthic compartments (2 & 6). This caused a considerable problem because the sediment residence time within the benthic compartments was so low that the priority pollutant was being flushed out of the system. This problem was corrected by routing a portion of the groundwater into the water column compartments (1 & 5). This increased the sediment residence time and thus, increased the concentration of adsorbed pollutant within the bed sediments. Figure 4.4 displays the effect of routing various percentages of groundwater through the benthic compartments for both configurations. Compartments two and four were not shown in configuration one because the residence time changed very

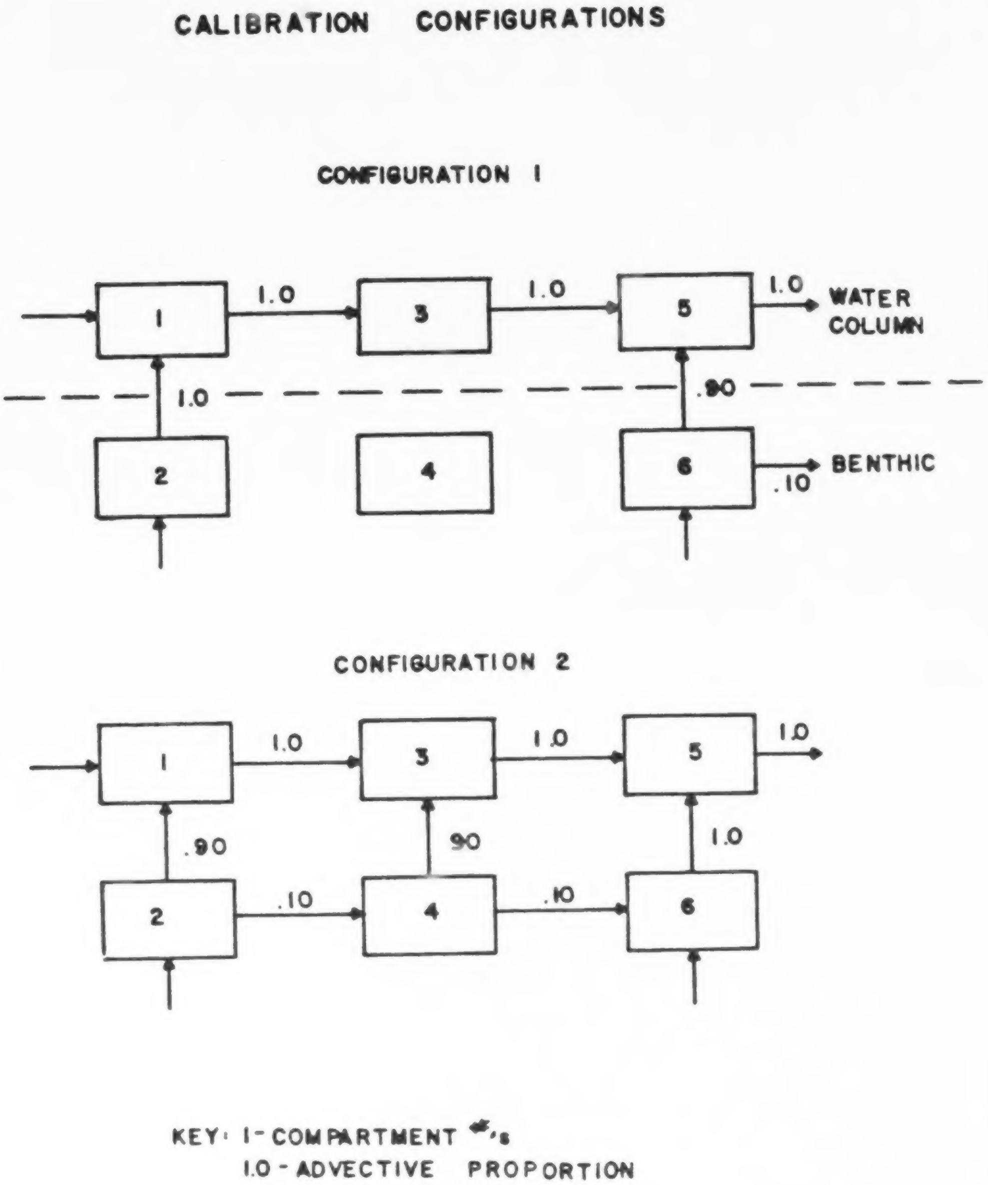

CALIBRATION CONFIGURATIONS
CONFIGURATION 1
1
2
3
4
5
6
1.0
1.0
1.0
1.0
.90
.10
WATER COLUMN
BENTHIC
CONFIGURATION 2
1
2
3
4
5
6
1.0
1.0
1.0
.90
.90
1.0
.10
.10
KEY: 1 - COMPARTMENT #'s
1.0 - ADVECTIVE PROPORTION

Figure 4.3 Calibration configurations.

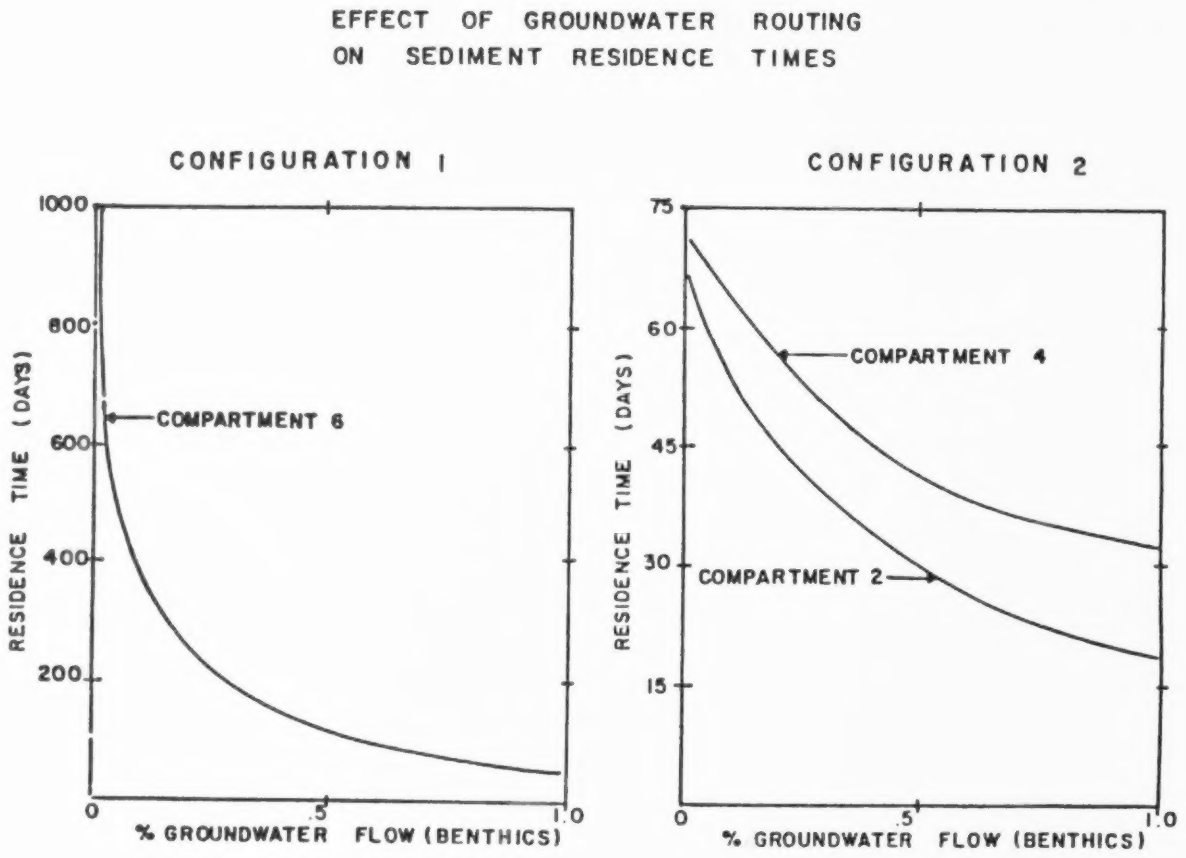


Figure 4.4 Effect of ground water routing on sediment residence times.

little. This slight change is a result of no flow being advected through these compartments. On the other hand, compartment six is not shown for configuration two because it also had very little change. Again, this is a result of no flow being advected through compartment six. At this point a decision was made to perform the remaining sensitivity analysis and calibration on configuration two.

### 4.7.3 Parameter Variation

The parameters which were manipulated during the calibration process included the advective pathway for groundwater accrual, the sediment Kd's and the dispersion coefficient.

The effect of the percent groundwater flow into the benthic compartments for configuration two allowed adjustment of the particulate concentration in the benthic regions (Figure 4.5). The next parameter adjusted for configuration two was the dispersion coefficient. This parameter was adjusted from 5.00*E-05 to 5.00*E-08 (m/hr2) to obtain the relationship between dispersion coefficient and adsorbed in the benthic compartments (Figure 4.6). The above range for dispersion coefficients should result from a calculation using the slope of the river bed, the magnitude of the diffusive exchange coefficients for the water column and the interstitial water, and the characteristic length of the gradient. A range of possible dispersion coefficients are indicated in Analysis of Fate of Chemicals in Receiving Waters - Phase I (DiToro and St. John, 1981).

The trend shown by varying the dispersion coefficient resulted in the sensitivity analysis of a final parameter. This parameter was the sediment Kd and originally it was not to be a calibration variable. The reason behind the change stemmed from the inability to simulate the measured adsorbed concentration within the benthic compartments. The decision to increase the Kd values from their field-determined values was reasonable considering the accuracy of benthic Kd determinations made in the field. It is very difficult to obtain a sediment sample without entrainment of water from the water column. The aqueous concentration of contaminant within the water column is much lower than that within the bed sediments, and the result would be a dilution of sediment interstitial concentrations. This dilution would result in a Kd value that was too low, and for this reason the Kd parameter has been changed to achieve higher particulate concentrations within the bed sediments. The adjustment of the Kd value and its effect on the benthic compartment adsorbed concentrations are shown in Figure 4.7.

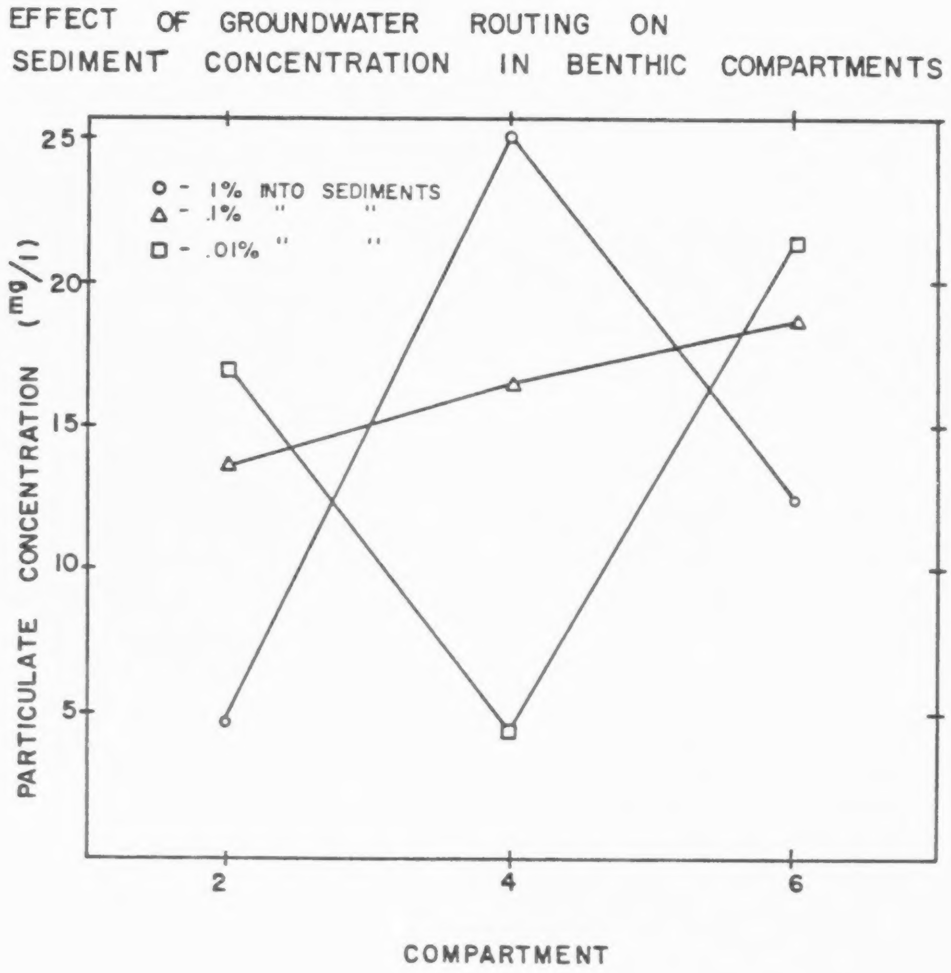


Figure 4.5 Effect of ground water routing on sediment concentrations in benthic compartments.

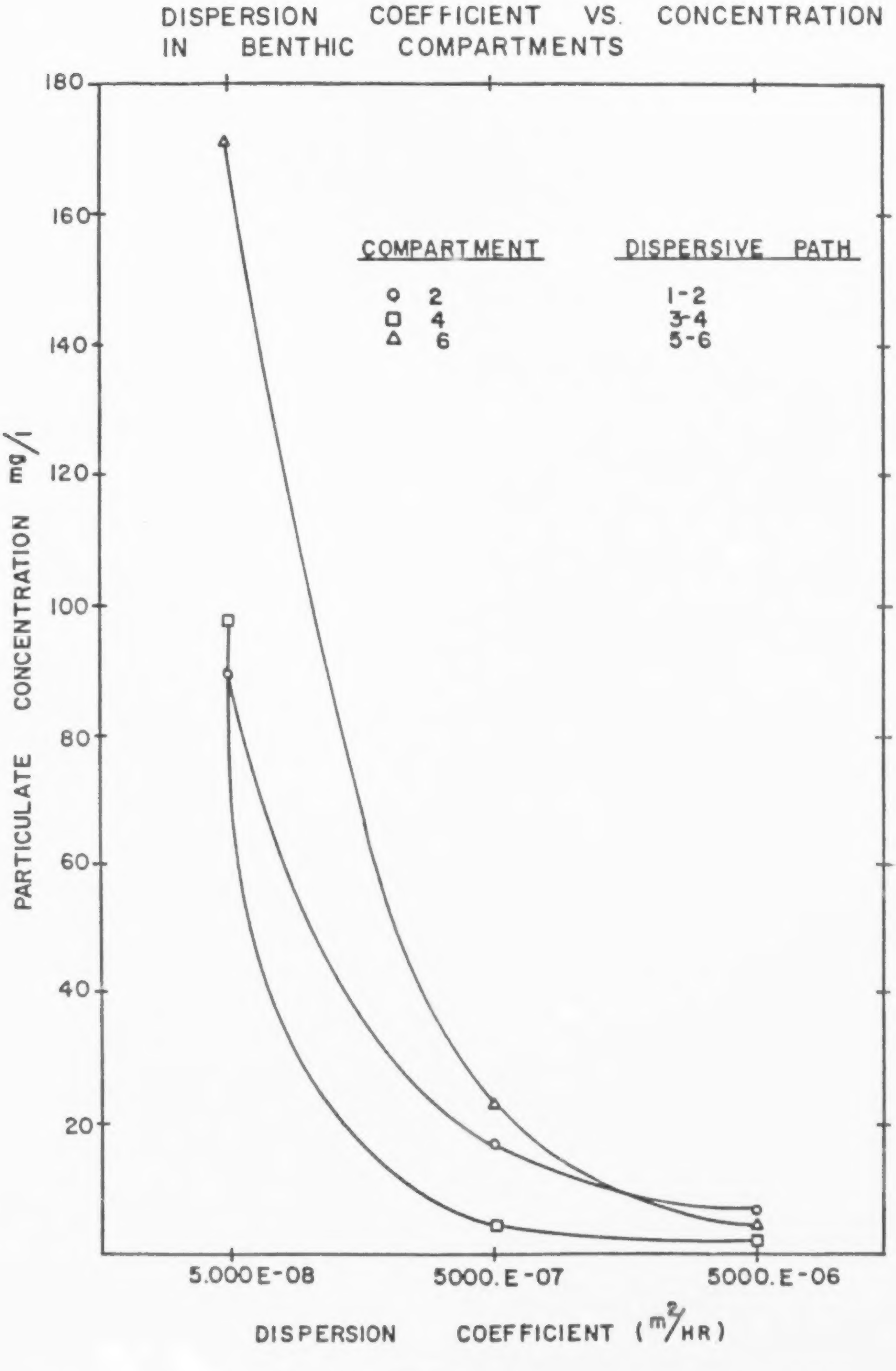


Figure 4.6 Dispersion coefficients vs. concentration of copper in the benthic compartments.

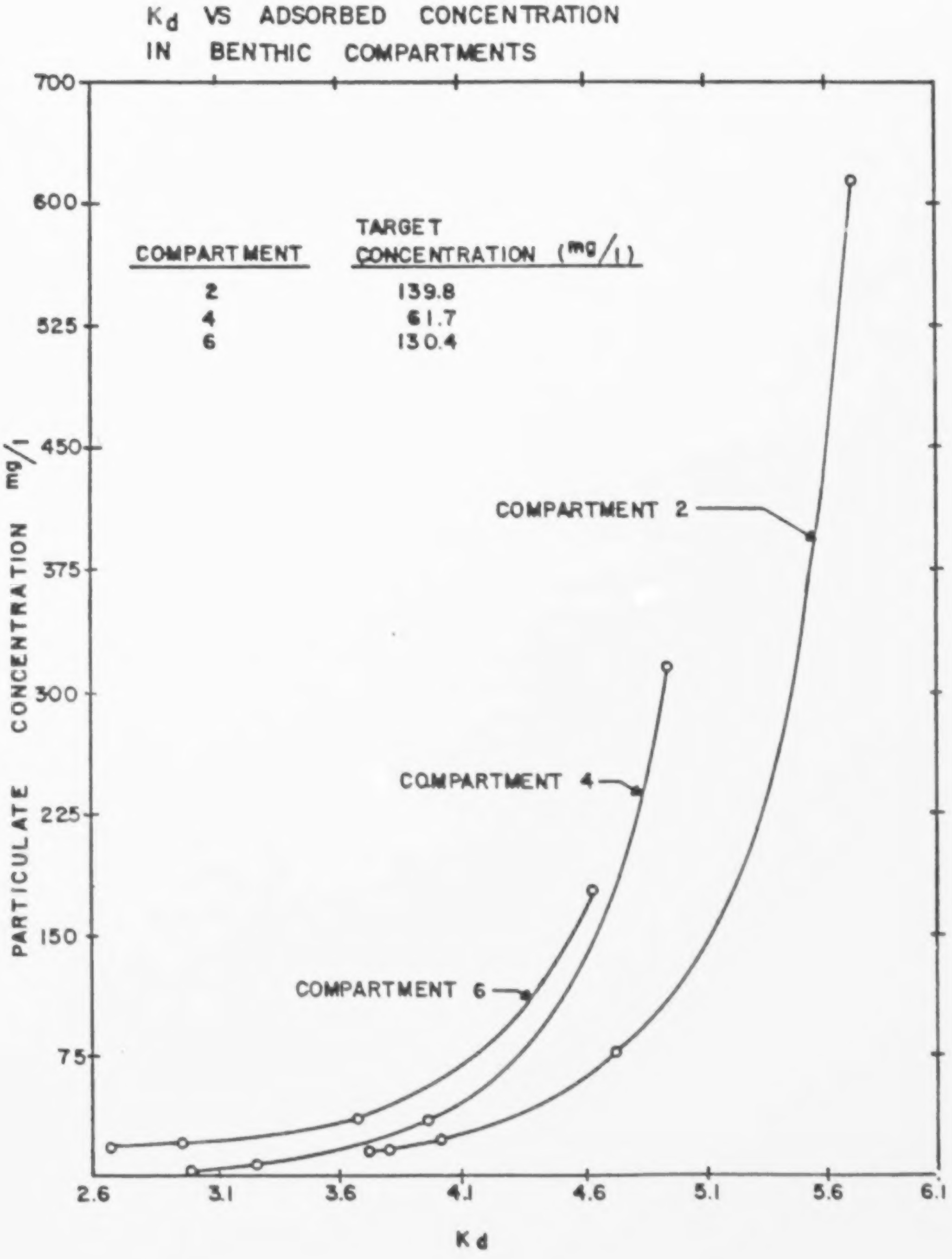


Figure 4.7 Kd vs. adsorbed concentration in the benthic compartment.

Another problem was encountered after the calibration of configuration two which resulted in a final adjustment of the advective pathways. The problem was that the total metal concentration in compartment five was too high, and to reduce this an advective pathway from the benthic compartment (compartment six) was established. The advective flow proportions from compartment six to compartment five were varied in an effort to reduce the total concentration in compartment five. The results obtained from varying the advective flow are presented in Figure 4.8. The measured concentrations for compartment five could not be obtained by varying the advective flow.

As a result of the inability to reduce the model error in compartment five, a ten compartment configuration was developed to better represent the Naugatuck River. This was reasonable considering that the model is based on a complete mix condition within each compartment, and the 6.7 mile compartment was so large that the concentration could not be lowered by adjusting any of the calibration parameters. The final ten compartment configuration is presented in Figure 4.9. The final configuration was calibrated by adjusting three variables; the percent ground water flow into the benthic compartments (8 & 10), the advective flow between compartments (8 to 7, and 10 to 9), and the Kd value for the benthic compartments. It is noted that these variables are difficult to determine in the field.

## 4.8 MODEL RESULTS

The model calibration was compared to an incremental flow model (Curtis, 1982) and laboratory results obtained from samples collected at various sites along the river. The two models being compared are slightly different, because the incremental flow model utilizes point source loads and groundwater as incremental loadings to an existing flow regime. The newly calculated concentration is then transported downstream. On the other hand, the MEXAMS model establishes instantaneous equilibrium with the point source load, and as a result, the model outputs are mean compartment outputs and not outputs at various points within the river reach. Thus, the MEXAMS model will not predict the concentration where a point load enters (Bogue Rd.), and the concentration measured will be higher than predicted.

The previous six compartment model calibration to particulate concentrations within the benthic compartments was very accurate. However, the model calibration to aqueous concentrations within the water column was not as accurate because compartment five concentrations were too high. The

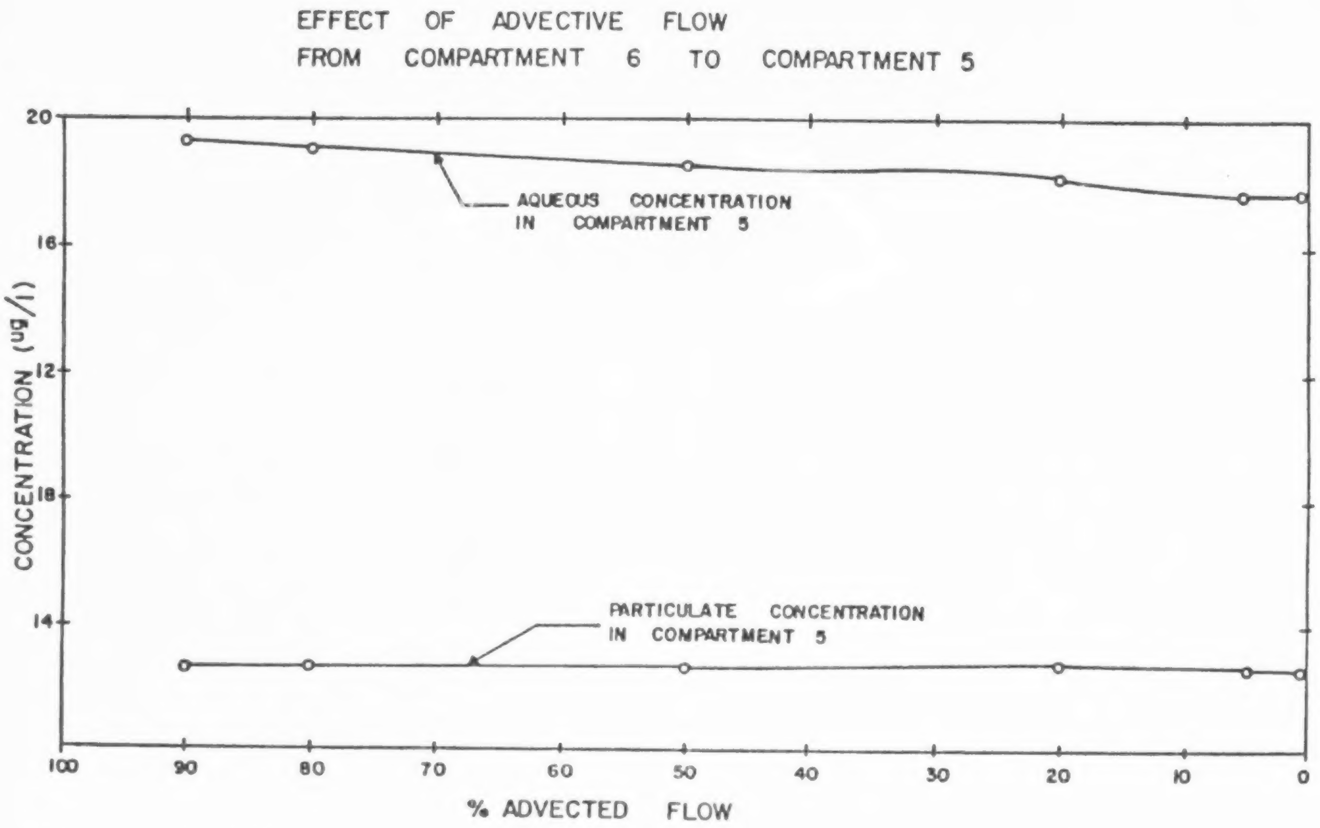


Figure 4.8 Effect of advective flow from compartment 6 to compartment 5.

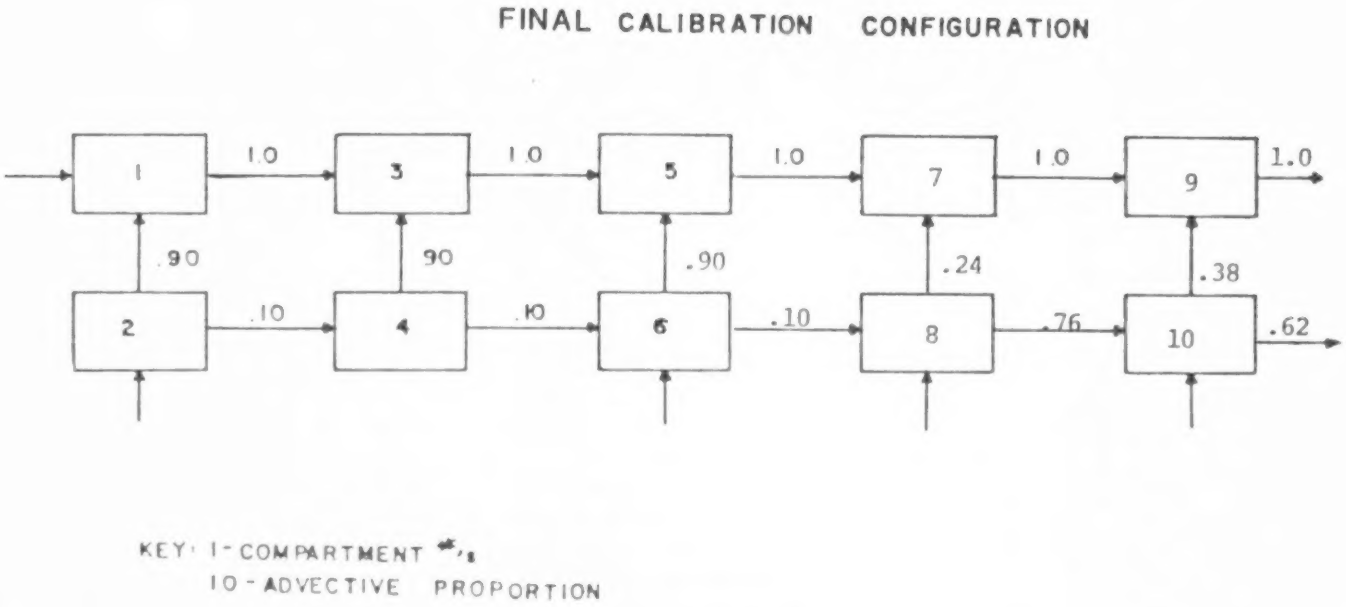

FINAL CALIBRATION CONFIGURATION
1
3
5
7
9
2
4
6
8
10
1.0
1.0
1.0
1.0
1.0
.90
90
.90
.24
.38
.10
.10
.10
.76
.62
KEY: 1-COMPARTMENT #'s
10-ADVECTIVE PROPORTION

Figure 4.9 Final calibration configuration.

six compartment model results are presented in Figure 4.10 and Table 4.15.

This model was improved by dividing the third river segment into smaller compartments. The compartmentalization of compartments five and six into smaller compartments would allow for a greater control of the model calibration. The third segment has been reconfigured by splitting compartments five and six in thirds. The calibration results obtained from the final configuration are presented in Figure 4.11 and Table 4.16, respectively. As stated previously, three parameters were adjusted to achieve a calibrated model. Table 4.17 displays the original log Kd's and the final log Kd's used to obtain the ten compartment calibration. The advective flow paths for the new compartmentalizations were presented in Figure 4.9, and the percent ground water routed into benthic compartments eight and ten were changed from .01% to .1% and .13%, respectively. The final calibration obtained for the ten compartment model was reasonable, and the concentrations predicted by the model were well within the error bars of the field data. A comparison of the model results to the model developed by the Connecticut State Department of Environmental Protection is shown in Figure 4.12.

## 4.9 EFFECT OF FUTURE LOADINGS

Since the purpose of this report is to illustrate the usefulness of the modeling system, the effect of an increase in metal loading to compartment one was simulated. This increase could be an additional discharger at some point in the future, or an increase in production by an existing discharger. The need for additional data and uncertainty analysis for model verification is again stressed to produce a tool which can be used with a certain degree of confidence. The existing contaminant loading is 1.284 E-02 Kg/hr and this was increased to 1.284 E-01 and 1.284 E+00. The effect of this increased metal loading on both water column and benthic compartments is displayed in Figure 4.13. This model, however, has some limitations, and they will be discussed in Section 8, along with recommendations for solving these drawbacks.

## 4.10 CONCLUSIONS

The behavior of total, dissolved and particulate (adsorbed copper within an 8.3 mile reach of the Naugatuck River (East Albert St. to Thomaston Bridge Abutment) was modeled using the Metals Exposure Assessment Modeling System (MEXAMS). Data

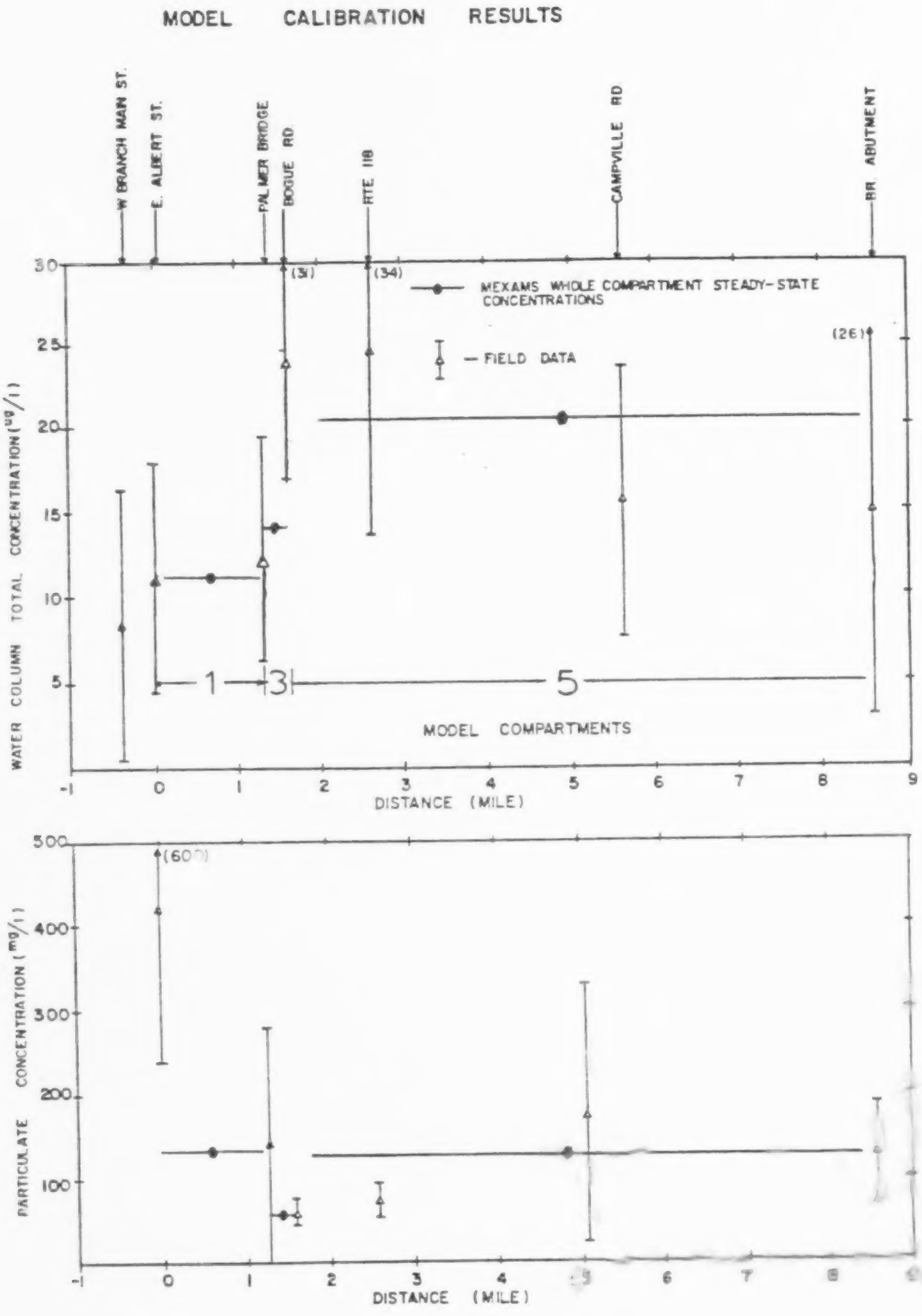


Figure 4.10 Model calibration results for the initial six compartment configuration.

TABLE 4.15 MODEL RESULTS FOR CONFIGURATION 3

| Location | Model Compartment | Total |  |  | Dissolved * |  |  |
|---|---|---|---|---|---|---|---|
|  |  | Field | Model | % Diff. | Field | Model | % Diff. |
| WATER COLUMN ( $\mu g/l$) |  |  |  |  |  |  |  |
| Palmer Br. Rd. | 1 | 12. | 11.5 | -4.1 | 9.5 | 9.1 | -4.7 |
| Bogue Rd | 3 | ------No Segment Data-------- |  |  | ------No Segment Data-------- |  |  |
| Rte. 118<br>Campville Rd.<br>Br. Abutment | 5 | 18.3 | 20.3 | +10.9 | 14.3 | 17.7 | +23.7 |
| BENTHIC REGION ( mg/l) |  |  |  |  | Particulate |  |  |
| Palmer Br. Rd. | 2 | 140. | 138. | -1.5 | 140. | 138. | -1.5 |
| Bogue Rd. | 4 | 62. | 59. | -4.8 | 62. | 59. | -5.0 |
| Rte. 118<br>Campville Rd.<br>Br. Abutment | 6 | 128. | 133. | +3.5 | 127. | 133. | +4.7 |

* The benthic region is shown as particulate copper in mg/l

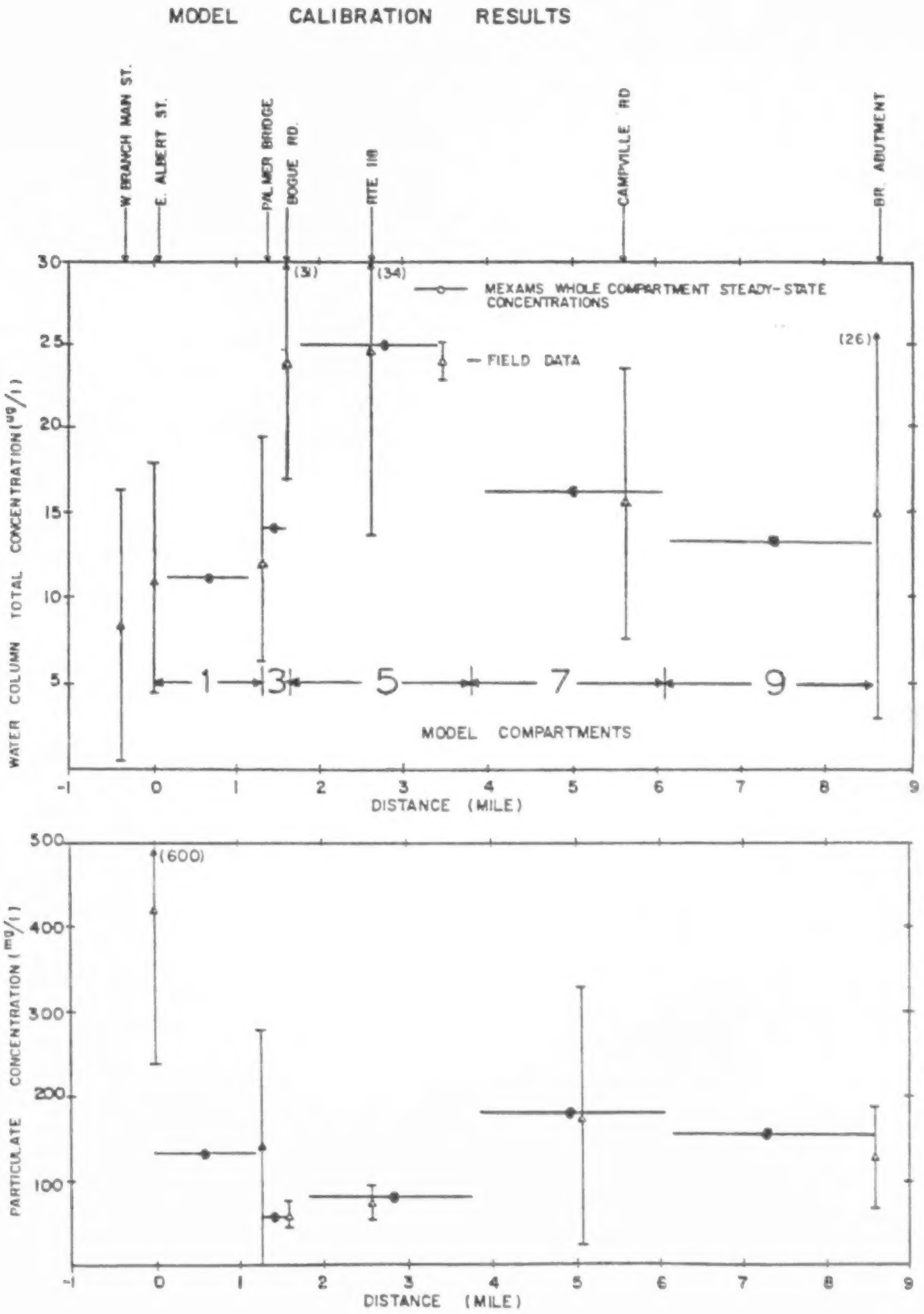


Figure 4.11 Model calibration results for the final ten compartment configuration.

## TABLE 4.16 MEXAMS - NAUGATUCK RIVER MODEL RESULTS

| LOCATION | MODEL COMPARTMENT | TOTAL COPPER |  | % | DISSOLVED COPPER |  | % |
|---|---|---|---|---|---|---|---|
|  |  | FIELD | MODEL | DIFF. | FIELD | MODEL | DIFF. |
| WATER COLUMN (μg/1) |  |  |  |  |  |  |  |
| Palmer Br. Rd. | 1 | 12. | 11.5 | -4.1 | 9.5 | 9.1 | -4.7 |
| Bogue Rd. | 3 | ------No Segment Data-------- |  |  | ------No Segment Data-------- |  |  |
| Rte. 118 | 5 | 24. | 24.6 | +2.5 | 17. | 16.8 | -1.2 |
| Campville Rd. | 7 | 16. | 16.6 | +3.8 | 14. | 14. | 0.0 |
| Br. Abutment | 9 | 14. | 12.6 | -10.0 | 11. | 10.6 | 3.6 |
| BENTHIC REGION (mg/1) |  |  |  |  | PARTICULATE COPPER |  |  |
| Palmer Br. Rd. | 2 | 140. | 138. | -1.5 | 140. | 138. | -1.5 |
| Bogue Rd. | 4 | 62. | 59. | -4.8 | 62. | 59. | -5.0 |
| Rte. 118 | 6 | 73. | 74. | +1.4 | 72. | 73. | +1.4 |
| Campville Rd. | 8 | 177. | 179. | +1.1 | 176. | 178. | +0.6 |
| Br. Abutment and Campville Rd. | 10 | 154.* | 150. | -2.6 | 154.* | 150. | -2.6 |

* The average copper concentration measured at Campville Rd. and the Bridge Abutment was used for comparison (based on model compartmentalization).

TABLE 4.17 COMPARATIVE Kd DATA

| Compartment # | Original log Kd | Calibrated log Kd |
|---|---|---|
| 1 | 0.30 | 0.30 |
| 2 | 3.72 | 5.02 |
| 3 | -0.25 | -0.25 |
| 4 | 2.95 | 4.20 |
| 5 | -0.05 | -0.05 |
| 6 | 2.67 | 4.42 |
| 7 | -0.05 | -0.05 |
| 8 | 2.67 | 5.30 |
| 9 | -0.05 | -0.05 |
| 10 | 2.67 | 5.17 |

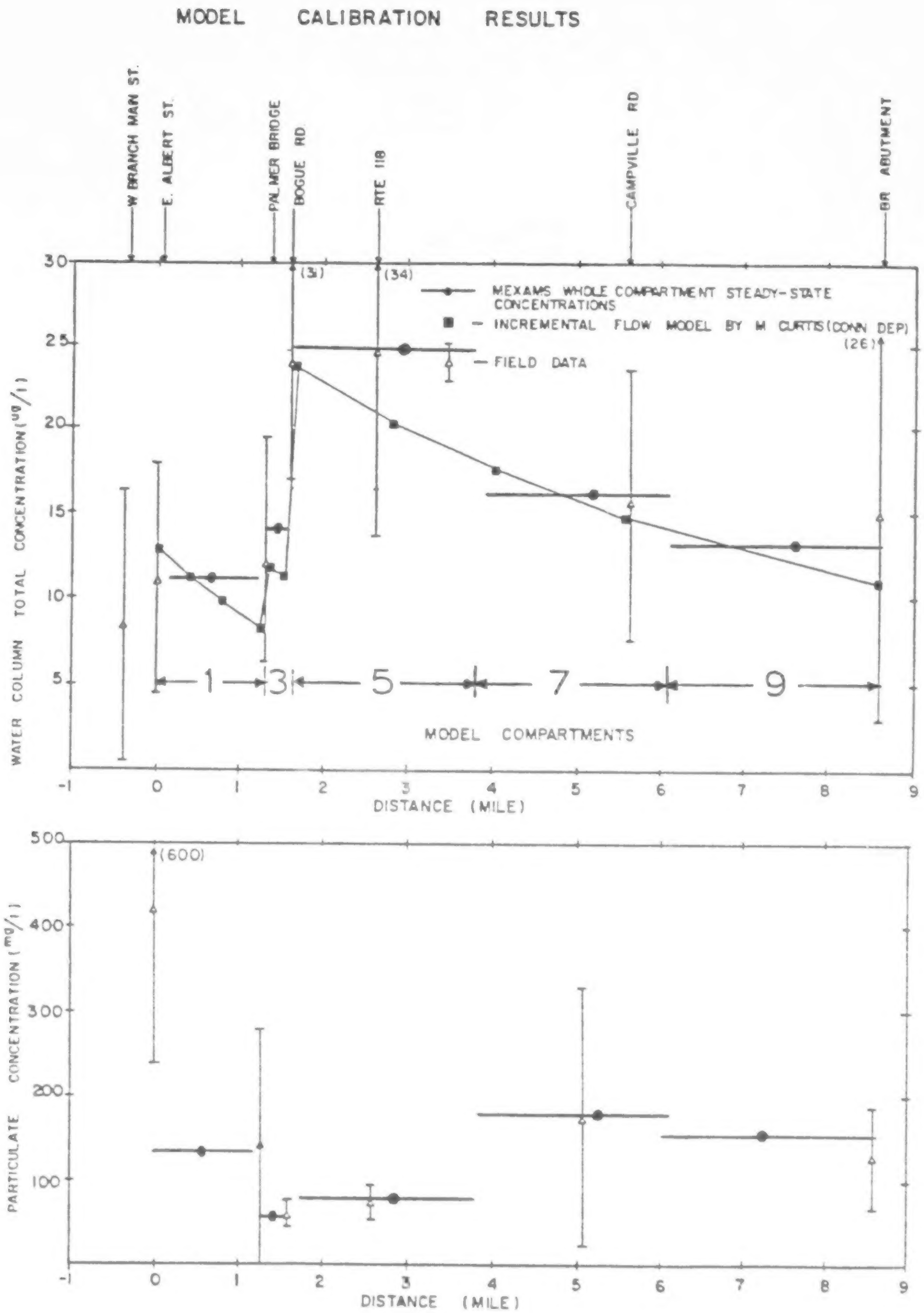


Figure 4.12 Model comparison to the incremental flow model developed by M. Curtis at the Connecticut Dept. of Environmental Protection.

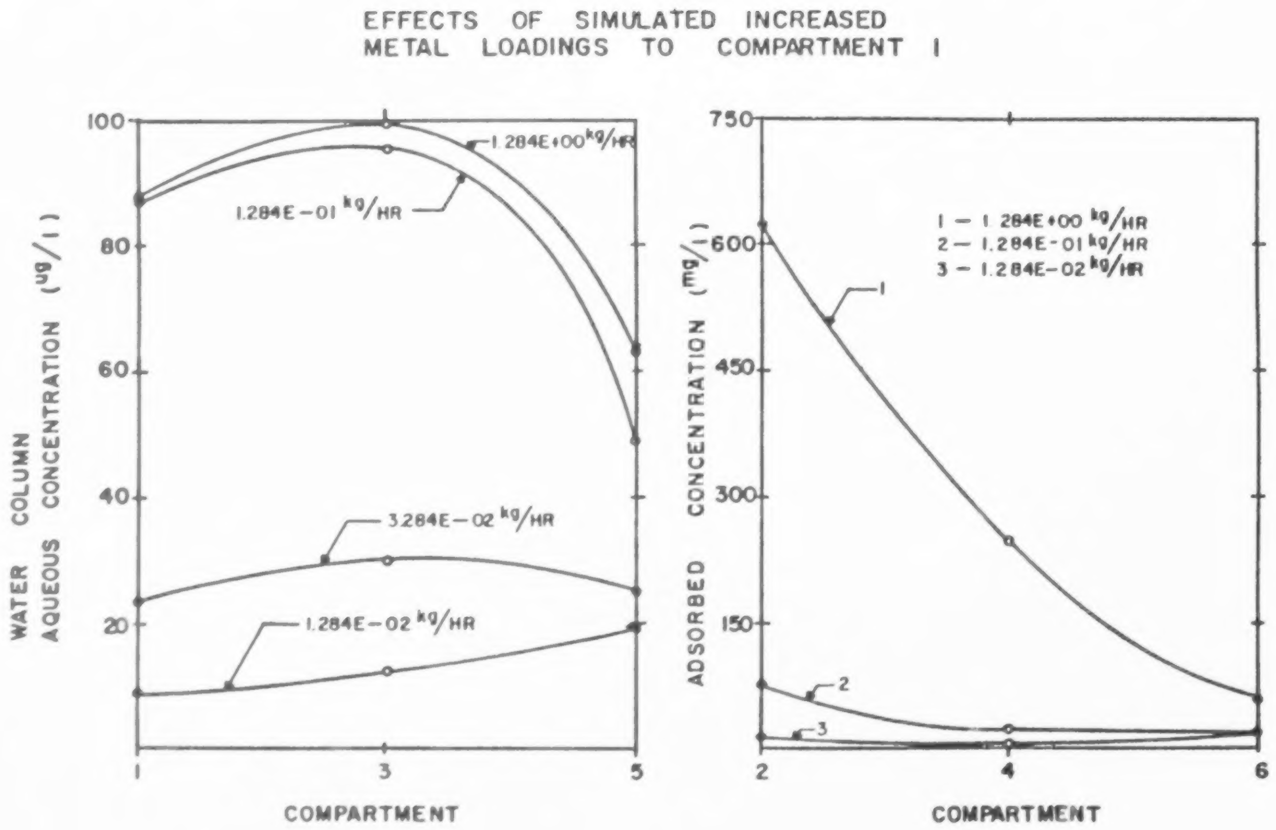


Figure 4.13 The effects of a simulated increased metal loading to compartment 1 on the metal calculations.

provided by the Department of Environmental Protection, State of Connecticut concerning mass metal loading, system physical and chemical characteristics was used to calibrate the MEXAMS computer model for this test case.

The most important aspect of this model calibration was the compartmentalization (configuration) of the river reach. The model was initially calibrated for a six compartment configuration. However, the six compartment configuration did not predict adequately (within 10% error) the total and dissolved concentrations in the furthermost downstream water column compartment (compartment five). The inability of the six compartment model to adequately predict the target (field) concentrations in compartment five was due to the length of the compartment (6.7 miles), and the fact that the model assumes complete mixing and creates instantaneous equilibrium within each compartment. As a result, a ten compartment configuration was used to obtain the final calibration. This configuration was obtained by dividing compartments five (water column) and six (adjacent benthic) into three equal compartments. This division achieved a greater compartment sensitivity to obtain the target (field measured) concentrations.

This final configuration (based upon the data provided) accurately calculated total, dissolved and particulate concentrations for all water column and benthic compartments. The major parameters adjusted to obtain this final calibration were the percent groundwater routed through the benthic compartments and the percent advected flow from benthic to water column compartments. The "activity" Kd's were kept at field determined values, while benthic Kd's were modified to reflect more realistic values (field determination of benthic dissolved and particulate metal level is difficult). However, the calibration of this model is only the initial phase of accurately modeling this river reach, and model validation to another data set is required.

# SECTION 5

# WHITE RIVER CASE STUDY

## 5.1 WHITE RIVER DESCRIPTION

The White River was selected for the testing of the MEXAMS computer model for the following reasons: 1) documented natural metal loading from an adjacent watershed 2) a well-developed chemical and hydrodynamic data base and 3) oil shale development in its drainage area.

Natural loadings of heavy metals into the White River system associated with tributary discharge result from periodic storm events. These discharges can result in dissolved metal concentrations that exceed the toxicity thresholds. It has been observed that dissolved copper concentrations were increased from 4 ug/l to 340 ug/l associated with an increase of river flow from 500 cfs to 1100 cfs due to a storm event in March, 1975. This elevated concentration of dissolved copper exceeds acute toxicity levels of the primary producers and macro-invertebrates (EPA, 1980). Elevated dissolved concentrations for Zn, Pb and Cr have also been observed (Medine, unpublished data). These periodic loadings due to storm events can cause natural alterations to the structure (Zanella, 1982) and function of the ecosystem (Medine and Porcella, 1980).

Previous research on the White River system conducted by the University of Colorado, White River Shale Oil Corporation and Ecosystem Research Institute has provided background data concerning seasonal chemical and hydrodynamic fluctuations (Table 5.1). Chemical data for several heavy metals, have been obtained from previous experiments to determine adsorption behavior, metal removal kinetics and speciation.

The White River drainage represents a system that is not extensively developed, although deposits of oil shale are presently being mined. This synthetic fuel development could represent a potential environmental alteration to the aquatic system (Stollenwerk and Runnells, 1981). The target metals chosen to exercise the MINTEQ adsorption model in this study

TABLE 5.1 THE CONCENTRATION OF SELECTED WATER QUALITY PARAMETERS FOR SEVERAL SURFACE WATER SOURCES TO THE STUDY SECTION OF THE WHITE RIVER (Source: WRSOC 1977)

Surface Waters

| | White River (09306500) | | | Evacuation Creek(1) (09306430) | | | Southam Canyon(2) (09306610) | | | Asphalt Wash(2) (09306625) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | mean±S.E. | max | min | mean±S.E. | max | min | mean±S.E. | max | min | mean±S.E. | max | min |
| Total Alkalinity(mgCaCO$_3$/l) | 181±4 | 250 | 107 | 371±11.14 | 450 | 98 | 164±15 | 189 | 119 | 139±32 | 189 | 39 |
| Dissoloved Solids(mg/l) | 491±16 | 913 | 213 | 3290±110 | 4710 | 753 | 579±150 | 990 | 260 | 642±240 | 1330 | 305 |
| Total Hardness(mg/l) | 270±6 | 440 | 140 | 1040±31 | 1200 | 250 | 147±34 | 220 | 84 | 144±35 | 230 | 68 |
| pH(units) | 8.14±.04 | 8.8 | 7.2 | 7.93±.04 | 9.0 | 7.3 | 8.0±.03 | 8.1 | 7.9 | 7.7±.4 | 8.0 | 7.4 |
| Conductance(umhos/cm) | 751±21 | 1290 | 290 | 4100±113 | 5800 | 1200 | 789±250 | 1480 | 330 | 1092±350 | 1920 | 418 |
| Sulfide(mg/l) | .148±.06 | 1.9 | 0.0 | .187±.07 | 2.0 | 0.0 | 0 | | | .10±.08 | 0.2 | 0 |
| Dissolved Organic Carbon(mg/l) | 5.57±0.7 | 9.9 | 2.9 | 14.4±2.2 | 35 | 6.2 | 8.50±2.5 | 12.0 | 5.0 | 13.0±.05 | 13.0 | 12.0 |
| Orthophosphate(mgP/l) | .017±.03 | .170 | 0.0 | .0104±.001 | .04 | 0.0 | .083±.03 | .09 | .08 | .08±.02 | 0.11 | 0.04 |
| Total Phosphorus(mgP/l) | .165±.03 | 1.10 | 0.0 | .0168±.003 | .11 | .001 | 7.90±2.4 | 14.0 | 1.8 | 23.0±12.0 | 40.0 | 5.90 |
| Ammonia(mgN/l) | .0298±.005 | .190 | 0.0 | .0316±.004 | .12 | .005 | .070±.010 | .07 | .06 | .045±.03 | .09 | 0.0 |
| Nitrate(mgN/l) | .103±.014 | .390 | 0.0 | .546±.09 | 1.8 | 0.0 | 2.40±.05 | 2.40 | 2.20 | 2.75±.45 | 3.40 | 2.10 |
| Nitrite(mgN/l) | .003±.001 | .010 | 0.0 | .610±.099 | 2.9 | 0.0 | 1.77±.25 | 2.40 | 1.40 | 2.47±.42 | 3.50 | 1.80 |
| Total Nitrogen(mgN/l) | .668±.089 | 3.30 | .10 | 1.59±.65 | 30.0 | 0.16 | 18.4±8.5 | 30.0 | 6.70 | 20.7±15.0 | 37.0 | 4.40 |
| Cu (ug/l) | 2.65±46 | 8.0 | 0.0 | 33.8±23 | 600 | 0.0 | 25±21.2 | 40 | 10 | 26.5±26 | 45 | 8 |
| Zn (ug/l) | 14.0±4.9 | 110 | 0.0 | 26.8±4.8 | 110 | 0.0 | 45±20 | 60 | 30 | 80±40 | 120 | 40 |
| Cd (ug/l) | .136±.074 | 1.0 | 0.0 | .08±.05 | 1 | 0.0 | 0 | | | 0 | | |
| Cr (ug/l) | 3.14±.95 | 10.0 | 0.0 | 6.2±1.7 | 30 | 0.0 | 1.0±.7 | 2 | 0.0 | 0 | | |
| Pb (ug/l) | .64±.26 | 5.0 | 0.0 | 1.16±.2 | 4 | 0.0 | 0 | | | 0 | | |
| Ni (ug/l) | 3.47±.79 | 12.0 | 0.0 | 4.84±.57 | 9 | 0.0 | 0 | | | 0 | | |
| Fe (ug/l) | 39.4±9.3 | 270 | 0.0 | 56.6±13.3 | 470 | 0.0 | 150±62 | 290 | 10 | 195±70 | 360 | 40 |
| Ba (ug/l) | 63.2±24 | 500 | 0.0 | 59.2±15.7 | 300 | 0.0 | 150±31 | 200 | 100 | 200 | 200 | 200 |
| Al (ug/l) | 20±4.1 | 120 | 0.0 | 20.0±4.5 | 110 | 0.0 | 77±45 | 180 | 0.0 | 100±25 | 160 | 50 |
| Mn (ug/l) | 4.79±1.3 | 30 | 0.0 | 103±15.6 | 320 | 0.0 | 7.5±2.5 | 10 | 0.0 | 93±70 | 260 | 10 |

---

(1) perennial
(2) ephemeral

(Zn, Pb, Ni, Cu) are associated with potential contamination to the lotic system from retorted waste shale leaching into groundwater and surface waters, retort processing waters, and mine dewatering activities (Chappell, 1984). Table 5.2 shows metal concentrations for 13 metals present in spent and raw shales (Medine, 1983). If leachate through groundwater or accidental discharge into the White River occurred, water quality standards established by the State of Utah (Table 5.3) could be exceeded, thus resulting in varying degrees of metal stress to the aquatic communities.

## 5.2 RIVER SEGMENT SELECTED FOR STUDY

The White River originates (upper basin) from the Flat Tops Wilderness Area (elevation: 3650 m.) in northwestern Colorado, which contributes the majority of the flow. The lower basin drainage area extends from northwestern Colorado to the confluence of the Green River in northeastern Utah. The lower basin area is characterized by a semiarid climate whose annual precipitation rarely exceeds 30 cm (Grant, 1983) and an annual evaporation of 90 cm (Bryson and Hare, 1974). The watershed is characterized by surficial deposits of lacustrine sediments containing calcite and dolomite deposited by Lake Unita (Palocene Epoch). It is the physical-chemical processes associated with the geologic weathering and erosional transport that causes drastic changes to water quality and gives the White River a strong carbonate system. The area of study on the White River is located in the lower drainage basin area in eastern Utah (Figure 5.1). The area is located near Federal Oil Shale Lease Tracts near Bonanza, Utah (elevation 1660 m.). The watershed associated with the study area is characterized by a gently sloping highly eroded plateau possessing steep wall canyons. Most of the upland soils (sandstone) supports Sagebrush-Greasewood, Shadscale, and Juniper vegetation. The Riparian habitat consists of Willow, Cottonwood and Bullrush (Grant, 1983). Due to the land morphology, the study area has various perennial washes and one ephemerial stream, Evacuation Creek.

Evacuation Creek, the only ephemerial tributary to the White River in Utah, represents a drainage area of 746 square kilometers. For several months the flow of this creek is low and very high in total dissolved solids. The headwaters consists of a groundwater discharge spring approximately 52 kilometers from the White River confluence. The watershed contains anthropogenic metal sources that are eroded and transported during storm events. This overland runoff can cause significant water quality changes to the White River by heavy metal and solids loading.

## TABLE 5.2 MAJOR POLLUTANTS IN OIL SHALE LEACHATES

| MAJOR INORGANICS (mg/ℓ) | | TRACE ELEMENTS (mg/ℓ) | |
|---|---|---|---|
| TDS | 140,000 | Hg | 0.005 |
| Na | 35,000 | Pb | 0.004 |
| Ca | 3,000 | Cd | 0.006 |
| Mg | 4,700 | As | 0.2 |
| K | 600 | Cu | 0.2 |
| $SO_4$ | 90,000 | Zn | 3.0 |
| Cℓ | 3,000 | Se | 2.0 |
| F | 17 | Fe | 2.0 |
| | | B | 10.0 |

| ORGANICS | |
|---|---|
| Oil & Grease | Unknown |
| Phenols | Unknown |
| TOC | 3-5% by weight |
| Benzene Extracts | 2,500 ppm (?) |
| Carcinogens | Unknown |

## TABLE 5.3 WATER QUALITY STANDARDS, UTAH/COLORADO

| Dissolved Constituent | Domestic Supply | Aquatic Life Protection<br>Utah[1]<br>3A/3B/3C | <br>Utah[1]<br>3D | <br>Colorado[2] |
|---|---|---|---|---|
| As | 0.05 | *[3] | * | 0.05 |
| Ba | 1.00 | * | * | * |
| Cd | 0.01 | 0.004[4] | * | 0.004 - 0.005 |
| Cr(VI) | 0.05 | 0.100 | .10 | 0.025 |
| Cu | 1.00 | 0.01 | | 0.005 - 0.01 |
| Fe | 0.30 | 1.00 | 1.00 | 1.00 |
| Pb | 0.05 | 0.05 | | 0.004 - 0.050 |
| Hg(total) | 0.002 | .00005 | .00005 | 0.00005 |
| Se | 0.01 | .05 | * | 0.05 |
| Ag | 0.05 | .01 | * | 0.00001-0.00015 |
| Zn | 5.00 | .05 | * | 0.05 - 0.10 |
| B | -- | * | * | * |
| F(Utah) | 1.4-2.4 | * | * | * |
| Ni | -- | * | * | 0.05 - 0.20 |

1) Standards for Aquatic Wildlife as of October 23, 1978
2) Standards for Aquatic Wildlife as of May 16, 1981
3) Insufficient Evidence to Warrant Standard
4) A Standard of 0.0004 mg/l was indicated for cold water game fish, i.e., Class 3A

Reproduced from
best available copy.

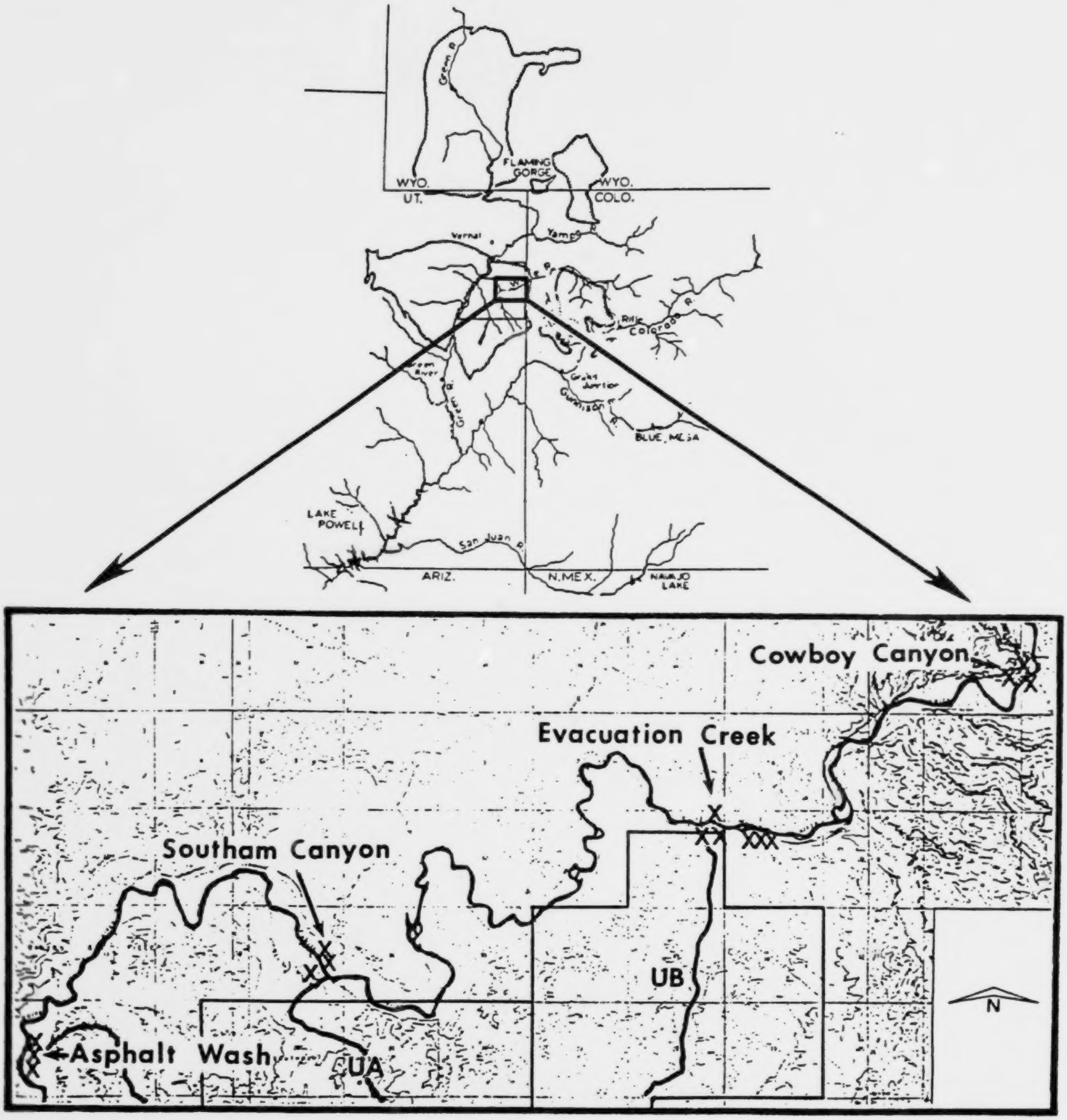

Green R.
FLAMING GORGE
WYO.
UT.
WYO.
COLO.
Vernal
Yampa R.
White R.
Rifle
Colorado R.
Green River
Green R.
Grand Junction
Gunnison R.
BLUE MESA
LAKE POWELL
San Juan R.
ARIZ.
N.MEX.
NAVAJO LAKE
Cowboy Canyon
Evacuation Creek
Southam Canyon
UB
N
Asphalt Wash
UA

Figure 5.1 White River study location.

The flows of the White River, which fluctuate seasonally, are correlated to three flow regimes, upper basin runoff, lower basin runoff and baseline. Upper basin runoff occurs generally from April through June, causing the highest flow conditions due to snowmelt conditions in the mountainous headwaters. Flows can vary from 14 to 77 m3/s. Lower basin runoff, usually from June to July characterizes intermediate flows (7.5 to 24 m3/s), where baseline regimes show the lowest flows (5.7 to 16.4 m3/s) from August through March (Figure 5.2).

Concentrations of major anions and cations found in the White River occur in the following order:

$$HCO_3^- > SO_4^{-2} > Cl^- > CO_3^{-2} > Ca^{+2} > Na^+ > Mg^{+2} > K^+$$

General water quality reflects the geological weathering, erosional input and evaporation-precipitation processes in the river. Water quality changes in terms of dissolved constituents varies directly with the three flow regimes. Upper basin runoff provides the best water quality conditions with low dissolved constituent concentrations but high total suspended solids concentrations. Lower basin runoff shows intermediate dissolved concentrations, where the baseline regime shows the highest concentration of dissolved substances and lowest total suspended solids values.

## 5.3 GENERAL WATER CHEMISTRY DATA DEVELOPMENT

The chemical matrix (major anions/cations) of the water system had to be determined for subsequent input into MINTEQ as Type I components. This matrix can be determined by three methods. One is to perform a full water quality analysis on the samples obtained from the field. This method can be both time consuming and expensive, if in-house laboratory facilities are non-existent. A second method is to obtain historical data compiled by the U.S.G.S. Water Quality Documents or from the EPA STORET SYSTEM. This method could be used if there is a strong comparison in major matrix constituents or in physical measurements such as electrical conductivity. The third way, and the one utilized for this study, is to obtain or formulate correlation graphs. These correlation graphs (Figures 5.3 & 5.4) show the relationship of the major anions and cations to a physical parameter (TDS). At least two years of constant monitoring of the system should be used to formulate the correlations, to encompass possible seasonal fluctuations. For example, field samples collected in August 1984 contained a total dissolved solids concentration of 535 mg/l and the major anions and cations were estimated using the linear equations for each graph:

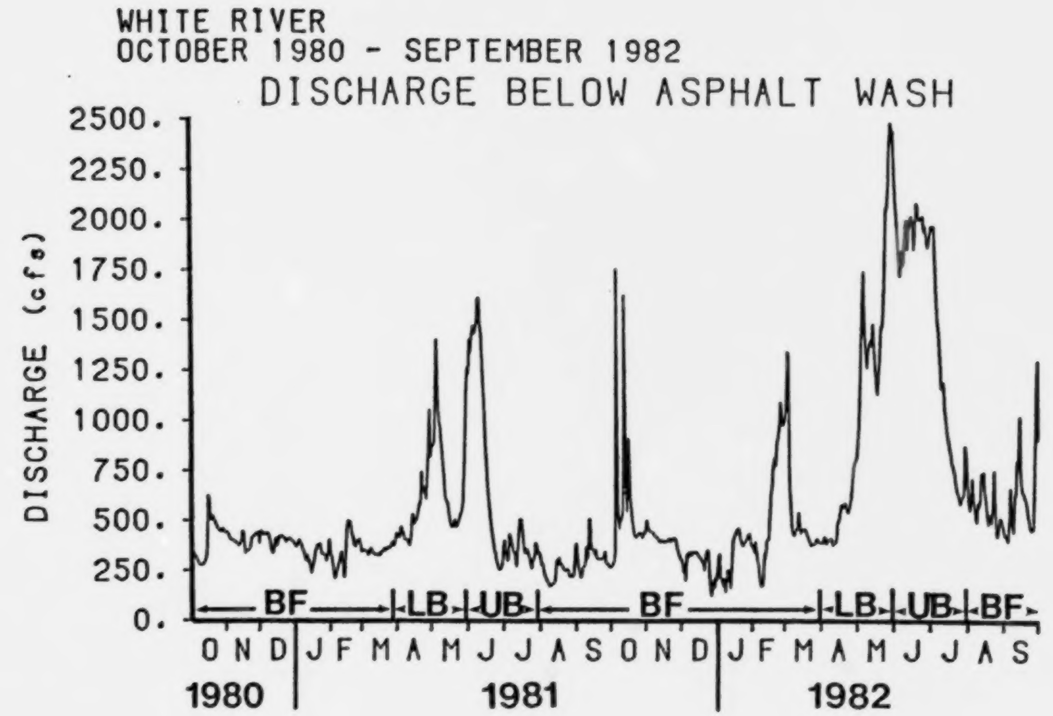


Figure 5.2 White River streamflow. (BF = base flow; LF = lower basin runoff; UB = upper basin runcff).

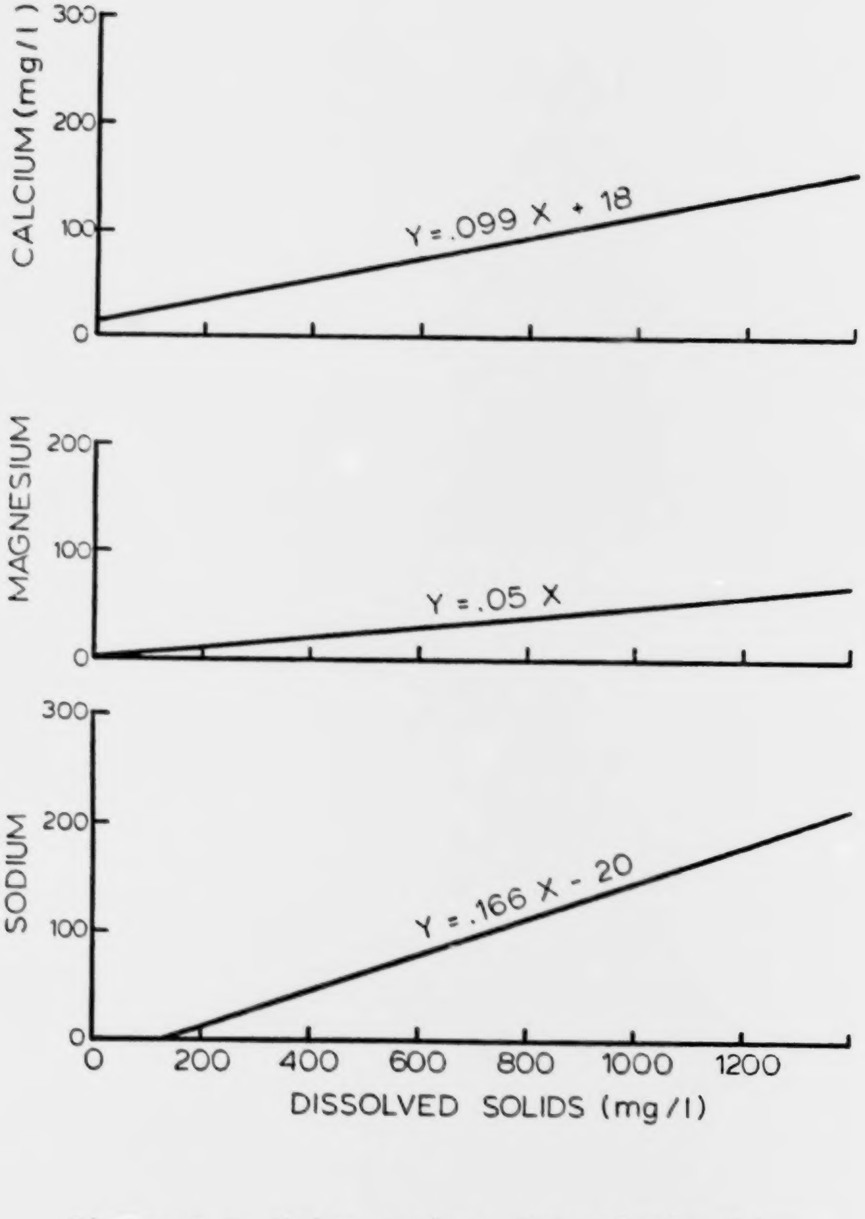


Figure 5.3 Major cation: TDS relationships.

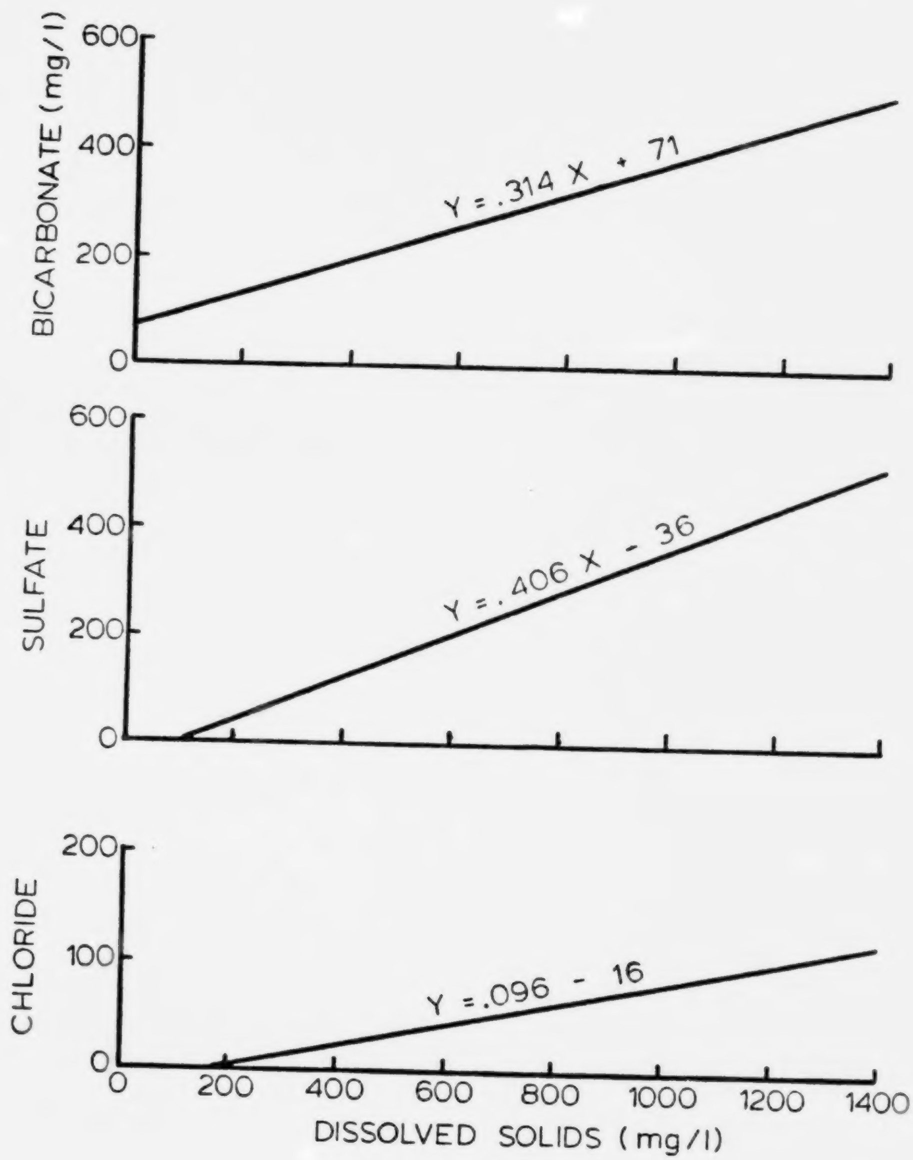


Figure 5.4 Major Anion: TDS relationships.

$HCO_3^-$ = 239 mg/l　　$Ca^{+2}$ = 71 mg/l
$SO_4^{-2}$ = 181 mg/l　　$Mg^{+2}$ = 27 mg/l
$Cl^-$ = 35 mg/l　　$Na^+$ = 69 mg/l

The remainder of the chemical matrix was obtained by using stated averages of historical data that were representative of the flow regime samples (Table 5.4).

Redox chemistries were not considered in the water quality matrix for several reasons even with the significant sulfide ion concentrations in the field data. Those reasons include the high dissolved oxygen concentrations; relative concentrations of ammonia, nitrate and nitrite; and low levels of ferrous ion observed. It was assumed that these conditions would reflect a high pe and that sulfide was rapidly being converted to sulfate. High sulfide levels were reported in alluvial groundwater of Evacuation Creek and Asphalt Wash.

## 5.4 ADSORPTION DATA DEVELOPMENT

To best utilize the capabilities of MINTEQ and MEXAMS for describing metal fate and transport, data are required to describe the solid phase partitioning of any potential metal loadings. In most cases, little data are available for suitable descriptions of sorption/desorption and chemical precipitation phenomena. There is a certain degree of caution which must be excercised in utilizing literature data to estimate metal partitioning to suspended solids and/or bed sediments. When using literature data or other sources of data not specifically collected on the system being modeled, it would be essential that the data reflect similar geology, water chemistry, sediment characteristics and other characteristics. At the extreme, this is illustrated by a comparison of literature data (using pure solid phases) to experimental data obtained on the White River (Figure 5.5). Natural sediments and suspended solids show very different metal removal as a function of pH, suspended solids concentration and initial metal level. This difference is due to the integrated characteristics of natural sediments which are a mixed population of solid types (oxides, clays, detritus, hydroxides, silicates, etc.). Site-specific data may be necessary, in many cases, for successful model application.

To illustrate how basic data may be acquired for site-specific application, adsorption experiments have been performed and the details reported herein. The objective of performing

## TABLE 5.4 DETAILED WHITE RIVER WATER QUALITY

| Selected Parameters | White River Surface Water Quality (11/1974-9/1976) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Baseflow | | | | Lower Basin Runoff | | | | Upper Basin Runoff | | | |
| | Mean | ± S. E. | Max | Min | Mean | ± S. E. | Max | Min | Mean | ± S. E. | Max | Min |
| Total Alkalinity (mgCaCo$_3$/ℓ) | 199 | ± 1.7 | 242 | 147 | 177 | ± 11.2 | 221 | 144 | 134 | ± 3.9 | 204 | 107 |
| Dissolved Solids (mg/ℓ) | 526 | ± 5.7 | 717 | 449 | 588 | ± 8.8 | 676 | 513 | 293 | ± 13.7 | 536 | 212 |
| Total Hardness (mg/ℓ) | 289 | ± 3.3 | 460 | 240 | 301 | ± 4.8 | 340 | 220 | 184 | ± 6.9 | 280 | 140 |
| pH (units) | 8.1 | ± 0.05 | 8.8 | 7.0 | 8.2 | ± 0.12 | 9.4 | 6.8 | 7.8 | ± 0.11 | 8.8 | 6.5 |
| Conductance (µmhos/cm) | 813 | ± 12.7 | 1650 | 625 | 874 | ± 13.7 | 1010 | 700 | 473 | ± 23.3 | 810 | 320 |
| Calcium (mg/ℓ) | 70 | ± 1.1 | 120 | 61 | 70 | ± 0.96 | 76 | 56 | 46 | ± 1.6 | 67 | 35 |
| Magnesium (mg/ℓ) | 27 | ± 0.4 | 39 | 22 | 30 | ± 0.6 | 35 | 20 | 16 | ± 0.9 | 28 | 11 |
| Sodium (mg/ℓ) | 71 | ± 1.9 | 180 | 34 | 82 | ± 1.9 | 110 | 65 | 32 | ± 2.5 | 75 | 17 |
| Potassium (mg/ℓ) | 2.3 | ± 0.09 | 6.1 | .9 | 2.3 | ± 0.28 | 4.0 | 2.0 | 1.7 | ± 0.07 | 3.0 | 1.3 |
| Chloride (mg/ℓ) | 40 | ± 1.3 | 120 | 24 | 41 | ± 1.2 | 58 | 25 | 15.5 | ± 1.5 | 42 | 3 |
| Sulfate (mg/ℓ) | 176 | ± 2.2 | 230 | 140 | 209 | ± 3.8 | 260 | 180 | 88 | ± 6.9 | 190 | 69 |
| Sulfide (mg/ℓ) | 0.2 | ± | 2.5 | 0 | 0.2 | ± | 1.3 | 0 | 0.1 | ± | .2 | 0 |
| DOC (mg/ℓ) | 6.8 | ± 1.18 | 14.0 | 2.5 | 5.8 | ± 1.39 | 12. | 3.0 | 5.8 | ± 0.53 | 8.6 | 4.4 |
| Orthophosphate (mgP/ℓ) | .02 | ± .01 | .87 | .00 | .01 | ± .002 | .04 | .00 | .02 | ± .004 | .06 | .00 |
| Ammonia (mgN/ℓ) | .03 | ± .004 | .19 | .00 | .05 | ± .013 | .29 | .00 | .02 | ± .004 | .04 | .00 |
| Nitrate (mgN/ℓ) | .12 | ± .02 | 1.10 | .00 | .14 | ± .029 | .52 | .00 | .16 | ± .02 | .38 | .01 |
| Cu (µg/ℓ) | 6.0 | ± 3.08 | 160 | 0 | 41 | ± 18.8 | 340 | 2 | 4 | ± 1.2 | 60 | 1 |
| 2N (µg/ℓ) | 21 | ± 5.07 | 180 | 0 | 12 | ± 3.7 | 60 | 0 | 4 | ± 1.5 | 20 | 0 |
| Cd (µg/ℓ) | 0 | | 1 | 0 | 1 | | 2 | 0 | 0 | | 1 | 0 |
| Cr (µg/ℓ) | 2 | | 20 | 0 | 2 | | 10 | 0 | 0 | | 0 | 0 |
| Pb (µg/ℓ) | 2 | | 7 | 0 | 4 | | 37 | 0 | 1 | | 4 | 0 |
| Ni (µg/ℓ) | 5 | | 16 | 0 | 2 | | 4 | 0 | 3 | | 6 | 0 |
| Fe (µg/ℓ) | 28 | ± 5.4 | 270 | 0 | 33 | ± 4.8 | 80 | 10 | 38 | ± 5.6 | 90 | 0 |
| Ba (µg/ℓ) | 48 | ± 15.8 | 140 | 0 | 38 | ± 10.2 | 100 | 0 | 27 | ± 14.5 | 130 | 0 |
| Al (µg/ℓ) | 17 | ± 2.2 | 80 | 0 | 30 | ± 5.7 | 90 | 0 | 30 | ± 4.4 | 80 | 0 |
| Mn (µg/ℓ) | 4 | | 20 | 0 | 9 | | 30 | 0 | 2 | | 10 | 0 |

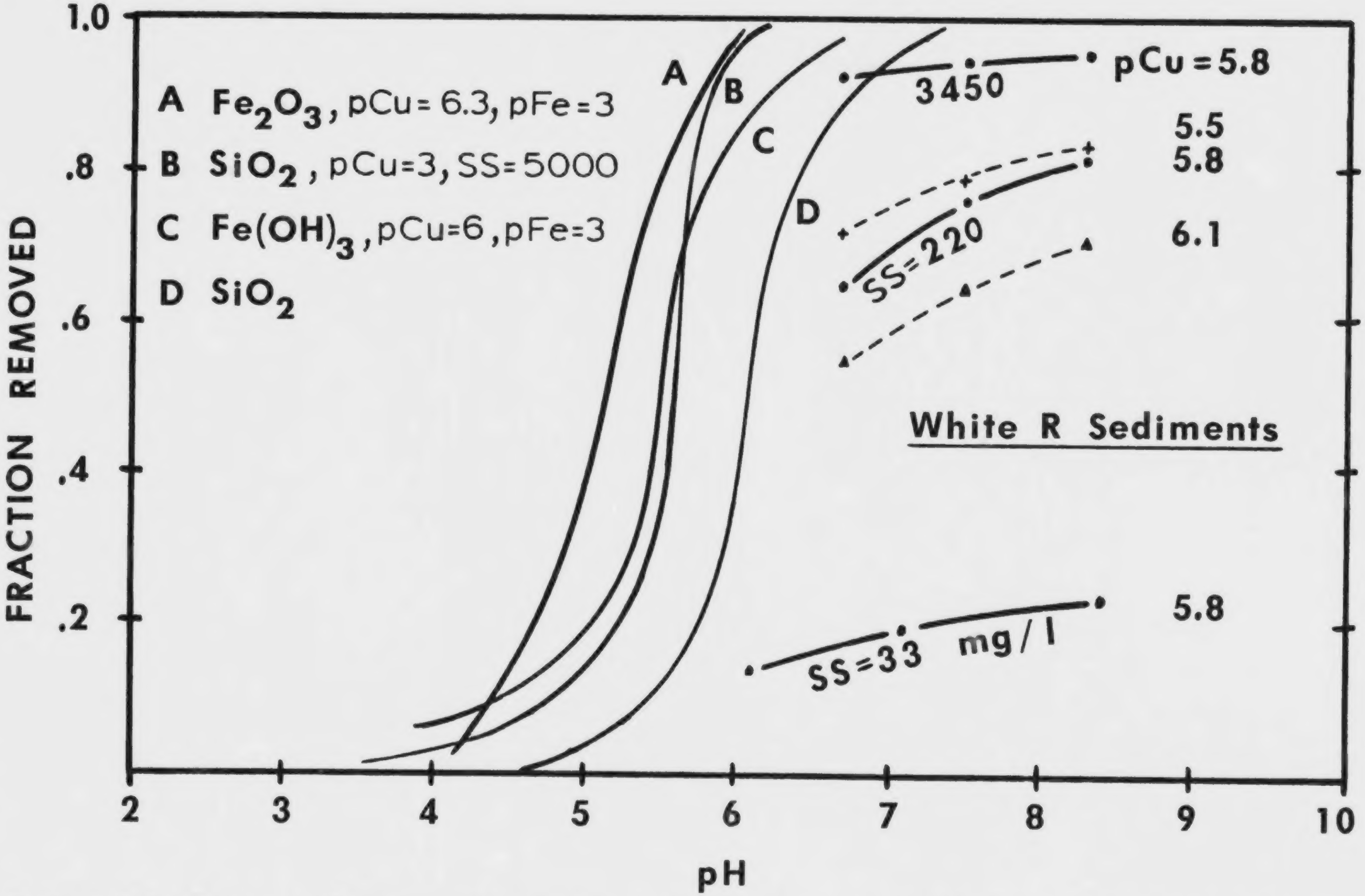


Figure 5.5 Summary of copper adsorption data showing a comparison of pure solid data to White River data. (pX=-logX, SS=suspended solids, A-Benjamin & Leckie (1981), D=Schindler et al (1976)).

laboratory reactor studies is to quantify equilibrium concentrations of dissolved and particulate metals, under controlled conditions. These equilibrium concentrations can be determined for various conditions such as varying pH, total metal concentrations, TSS concentrations, ionic strengths and matrix concentrations. By varying parameters, adsorption dynamic relationships can be analyzed and formulated for MINTEQ input.

Two reactor techniques were used for determining adsorption behavior for target metals; small volume reactors and large volume reactors. Both of these techniques used ambient solids concentration and ionic strengths. The parameters varied were total metal and pH. The small volume reactor method was used for samples representative of upper basin runoff conditions (March, 1984). The target metals run using this technique were Cu, Pb and Ni.

Selected pH values used for the reactor experiments were chosen for two reasons, one was to encompass the White River's seasonal pH fluctuations and the second was to observe metal speciation and adsorption trends. For example, reactor experiments for Cu were performed at pH values of 6.80, 7.46, 8.31 (ambient) and 8.95. To each specific pH treatment, five different total metal concentrations, that would encompass probable tributary load discharges were introduced (five separate reactors); 25 ug/l, 50 ug/l, 200 ug/l, 500 ug/l and 1000 ug/l.

Two field sampling trips were taken to the White River on March 22 and August 14, 1984 to obtain samples representative of upper basin and baseline runoff regimes, respectively. Field and laboratory samples for both trips were obtained at the U.S.G.S. Gaging Station (see Figure 5.1). Field grab samples were collected approximately 10 meters from shore in previously acid-washed 1 liter Nalgene bottles. The samples were shaken and aliquots were transferred for total suspended solids, total metal and dissolved metal samples. Dissolved metal samples were obtained by immediate filtration through .45 micron filter with subsequent nitric acid preservation. pH analyses using a portable pH meter (Orion 399A) and a two buffer standardization (7 & 10) were performed on site.

For samples to be used for laboratory experiments, two 120 l polypropylene containers were used to transport bulk samples back to Boulder, Colorado. These containers were filled by obtaining several grab samples, using acid washed, 20 l Nalgene carboys. The containers were covered and directly transported to the University of Colorado's Environmental Engineering Laboratory (7 hours) and refrigerated at $4^{\circ}$ C.

The refrigerated bulk sample was allowed to come to laboratory room temperature (25° C) before homogenizing the sample. A large vortex mixer was placed inside the polypropylene container and allowed to stir for approximately thirty minutes. Six liters of the bulk sample were transferred to a 9 liter lucite cylinder with an outlet port 7 mm from the bottom lucite base plate. The cylinder was elevated on a support assembly so a magnetic stirrer could be utilized. A 5 mm magnetic stirring bar provides less than satisfactory solids homogeneity and so a small laboratory vortex mixer with teflon stirring paddles was used to supplement mixing. 100 ml samples were volumetrically withdrawn from the mixing cylinder and placed in previously acid washed 125 ml polypropylene sample bottles. In addition, random samples were collected for TSS determinations to test for homogeneity. The collected samples were then pH adjusted using 3N HNO3 and NaOH to predesignated pH values using a Ross Combination Electrode and an Orion 399A pH meter (two buffer standardization). Due to the high alkalinity of the White River, a preliminary test was performed to determine how much acid or base should be added to obtain a desired pH value 24 hours later. Samples were then spiked with varying concentrations of primary metal standard to obtain designated total metal levels.

To insure no metal loss due to sample container adsorption, a preliminary test was performed, adding 5000 ug/l of target metal (Pb, Cu, Ni) to separate containers filled with White River water. The samples were allowed to sit 48 hours and then were discarded. The containers were rinsed twice, then filled with Milli-Q reagent grade water and then acidified with HNO3. Atomic absorption analysis for all target metals showed less than .01% container adsorption.

The samples were placed on a wrist action shaker for 12 hours, when it was assumed that equilibrium condition prevailed from previous kinetic data. Final pH determinations were performed and then 50 ml portions of the samples were filtered through a .45 micron filter and poured back into the same sample container that had been previously twice rinsed with Milli-Q water. Dissolved and total metal samples were preserved with nitric acid and refrigerated at 4° C.

The Large Volume Reactor technique was used for bulk samples collected on the August field sampling trip, involving the target metal, Zn. The reactors used were four lucite cylinders (60 mm x 14 mm) each with a total volume of 9 liters. Outlet ports were located 7 mm from the bottom lucite baseplate.

Refrigerated bulk samples were allowed to achieve laboratory room temperature (25° C) before homogenizing the sample with the large vortex mixer. The sample was stirred for 30 minutes, then 1 liter samples were taken volumetrically and poured alternately into the reactors until a final volume of 4 liters was achieved. The alternate pouring was used to minimize TSS heterogeneity. The reactors were elevated on a support structure so that magnetic stirring bars/plates could be utilized.

The pH ranges selected for these zinc reactor experiments were 6.7, 7.5 and 8.4 (ambient). The total metal levels used were 100 ug/l, 200 ug/l, 500 ug/l and 1000 ug/l (including a control). In order to perform reactor tests at pH values other than ambient, a pH stabilization period was required. During this time, in-situ pH measurements were made and appropriate amounts of 3N HNO3 were added to obtain the desired pH value. These measurements were taken, when possible, every two hours for 48 hours. Due to this stabilization period, pH shifts over time were less pronounced, thus causing less of a metal adsorption-desorption effect when the experiment was performed.

Since no previous kinetic data were available to determine the time to chemical equilibria, a time series experiment was performed on the pH 7.5 reactor tests. Samples from the reactors were taken at the following time intervals, after metal addition: 5 min., 10 min., 30 min., 1 hr., 2 hrs., 4 hrs., 8 hrs., 24 hrs., 48 hrs. The samples taken at these specific intervals were immediately filtered through a .45 micron filter and HNO3 preserved for atomic adsorption analysis. After target metal addition (for all pH series experiments), the reactors were stirred constantly and pH was monitored every two hours for 48 hours, when possible. At the time of equilibrium, samples were taken for dissolved, total metal and TSS analysis. Results of the time series test are shown in Figure 5.6, and it was concluded that 48 hours were necessary to achieve equilibrium conditions.

Previous adsorption experiments on the White River using copper as the target metal indicated that nearly 24 hours were required to achieve equilibrium conditions (Figure 5.7). The range of suspended solids concentrations in the tests were 100-400 mg/l, the initial dissolved copper concentration was 52 ug/l and the pH was held at ambient (8.20). Parallel studies with lead indicated that equilibrium was reached in about four hours. From these results it is apparent that the equilibrium time is related to the affinity of the surface sites for the particular metal, following the sequence generally observed for divalent metal partitioning to solid phases. It was also noted that equilibrium time was inversely proportional to the concentration of suspended solids in the range 100-3500 mg/l. At the highest concentration of suspended solids (upper basin runoff and storm events), equilibrium was reached in 1-3 hours for Pb, Cu, Zn, and Ni.

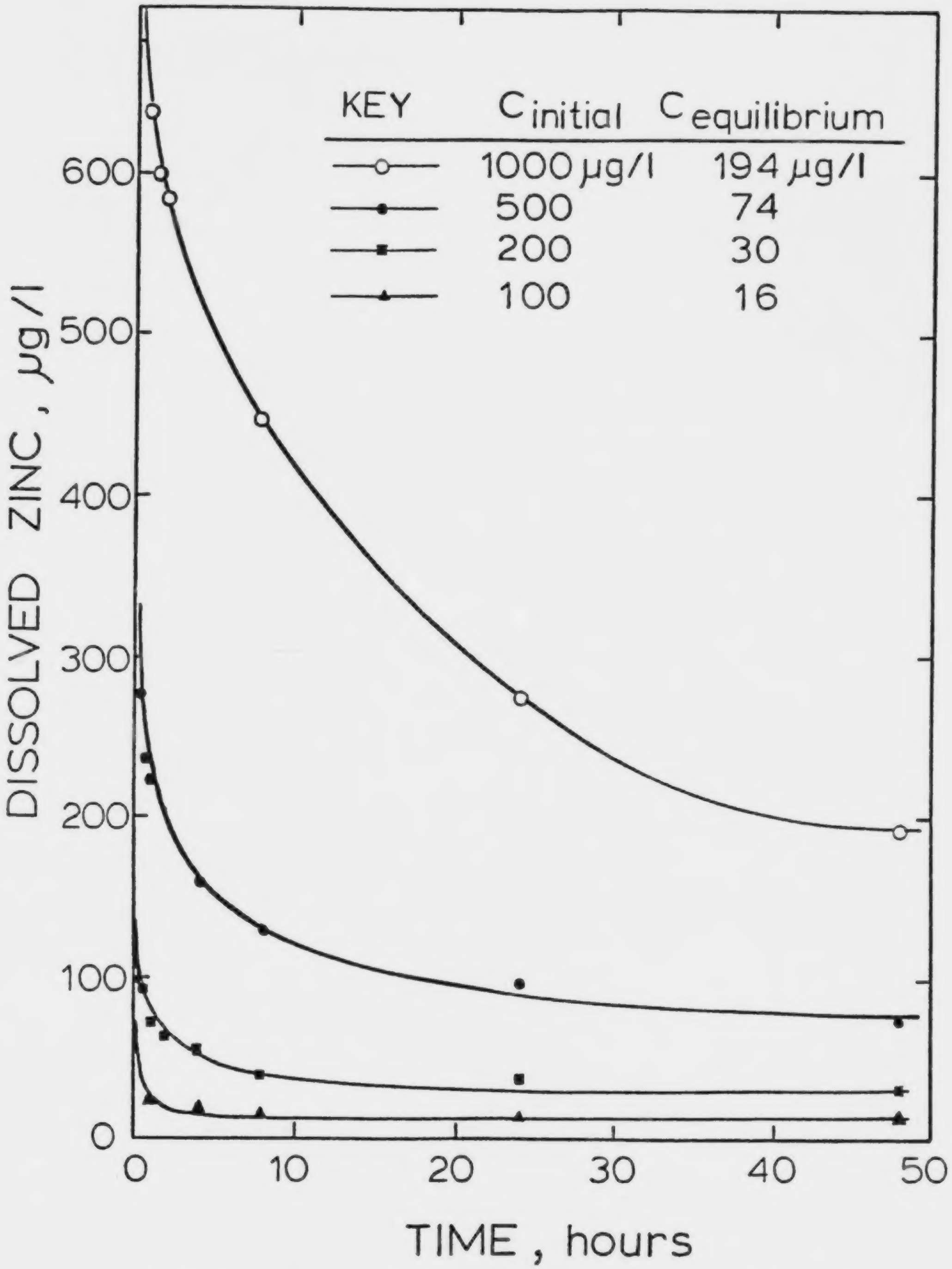


Figure 5.6 Zinc adsorption kinetics, pH=7.50

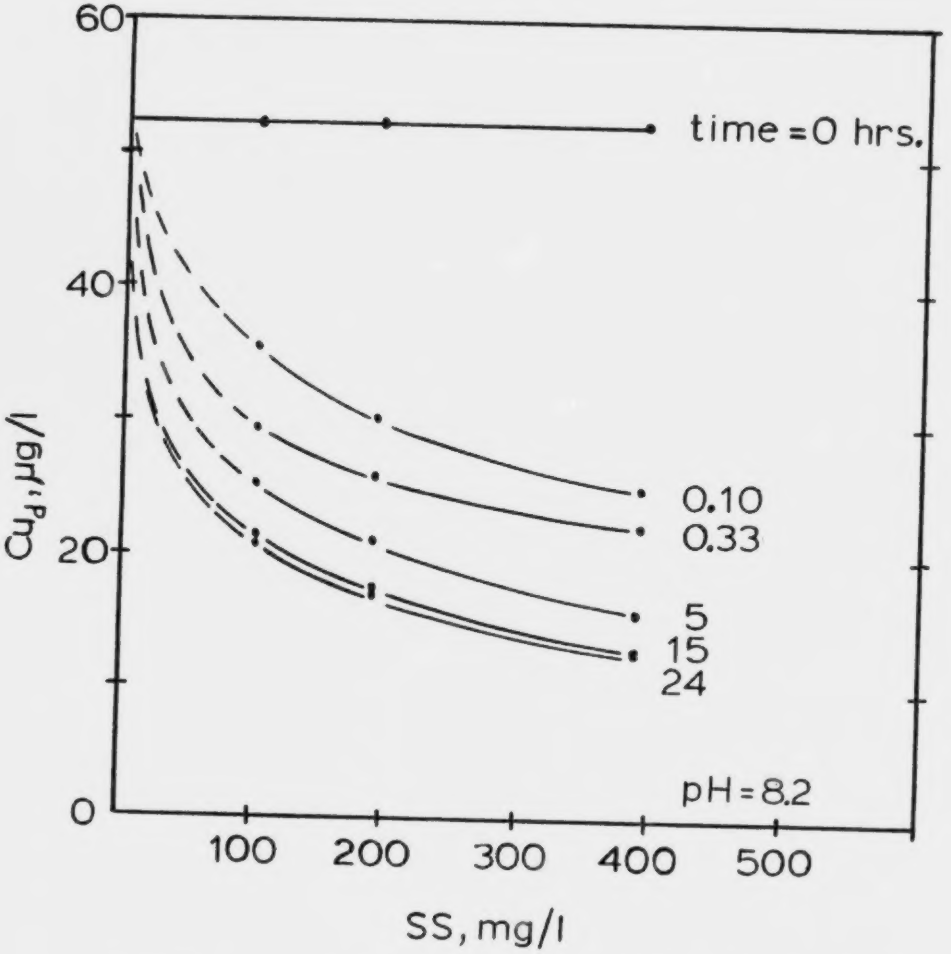


Figure 5.7 Copper adsorption kinetics, pH=8.20.

In summary, the advantage of the small volume reactor method was that a whole set of pH/total metal tests for a target metal could be set up in a short amount of time. The method, requiring less sample and pH monitoring, may be implemented in field situations where temporary field laboratories are utilized. One of the disadvantages to the small volume reactor technique was the heterogeneity of total suspended solids concentrations found in random samples. Concentration values ranged from 2086 mg/l to 1496 mg/l for 19 samples, with a mean value of 1564 ± 210 mg/l. In comparison, the field grab sample TSS concentration was 1652 mg/l resulting in a 5% difference. The second disadvantage was the precision obtained in adjusting the samples to specific pH values. Of the four pH sites that required adjustment, three had a relative standard deviation of 2% or lower and one set has RSD values from 7%. In only one instance did the difference exceed .3 pH units, which can be critical in dealing with adsorption experiments. This problem was probably due to the heterogeneity of the samples, that can occur when dealing with 100 ml subsystem environments.

The main advantage of the large volume technique was that the experimental system was easier to control, resulting in improved precision in total suspended solids concentrations for all reactors and more control over pH adjustments. Out of 15 large reactor experiments, the total suspended solids concentration was 619 ± 29 mg/l (RSD of 5%), and compared well to a field grab sample value of 590 mg/l. In situ pH measurements gave more control in adjusting reactors to specific values. Although the pH of the reactors did tend to drift due to the White River's alkalinity, the pH value did not exceed .05 pH units from specified values at any time. The disadvantages of this procedure were: time required for reactor pH stabilization, constant in-situ pH monitoring, large volume of sample required and the long period of time required to finish a given set of experiments.

In this study, no analytical digestion techniques were used to determine total metal concentrations. Instead, total metal samples obtained from the field and laboratory experiments were acidified with nitric acid to a pH below 2. This acidic environment was assumed sufficient to release sorbed metals from suspended solids. This approach is environmentally realistic, in the sense that most aquatic systems do not naturally undergo intense heat and acidic conditions inherent in digestion techniques. A pH of 2.0 (that may occur in benthic regions where organic material is undergoing decomposition) should release metals that have charged interactions at solid surfaces and not metals bounded internally in a solid's lattice structure. This bounded metal is highly unlikely to be involved in contributing to dissolved metal concentrations to the river system.

The manner in which the aqueous and particulate phase metals are classified (or speciated) is currently the subject of considerable research activity, and, beyond the scope of this report. However, additional information regarding labile and non-labile forms of metal is necessary to improve our abilities to describe metal transport, fate and biological consequences. Sequential processing of aqueous samples using filtration, Anodic Stripping Voltametry (ASV), Chelex-100 and UV radiation can provide much information concerning the types of metal species present. Sequential sediment or particulate phase extractions along with an analysis of particle size and general characteristics (organic matter, clay content, etc.) can yield information concerning metal associations with organics, clays, reducible phases, humic acids, detrital silicate and others (Forstner and Wittmann, 1981) and contribute to an understanding of metal removal processes and the availability for release to aqueous forms.

Trace metal analysis was performed for Cu, Pb, Zn and Ni using an Instrumentation Laboratory 551 Atomic Adsorption Spectrophotometer, utilizing a Graphite Furnace (IL 555) and Fastac autosampler (IL 254). For all metal analysis, deuterium background correction was used. For total metal samples an Instrumentation Laboratory 151 utilizing an air-acetylene flame with deuterium background correction was used.

## 5.5 MINTEQ DETERMINATION OF METAL ION ACTIVITY

The MINTEQ program has a large amount of flexibility in the way the user defines the chemistry of the aquatic system being modeled. The first procedure in implementing MINTEQ for activity determination is to develop an input file without considering adsorption and chemical precipitation. The input file contains the following information: 1) an alphanumeric description of the computer run, 2) specific information concerning system temperature, analytical units adsorption routines and input-output options, 3) Type I components (major/minor ions), 4) Type III species (fixed activities).

As seen from the input file example for Zn in Table 5.5, the first two lines are alphanumeric descriptions of the sample, laboratory conditions and the computer run. Line 3 represents the laboratory system temperature used when performing adsorption experiments, and the analytical units of the Type I component (mg/l). Line 4 contains eight run specific user options: inorganic carbon input (0 = total inorganic carbon), debug printing, charge balance (1 = termination of program if

## TABLE 5.5 MINTEQ INPUT FILE-AQUEOUS ZINC SPECIATION

```
WHITE RIVER..AUGUST SAMPLING..ZINC ACTIVITY..PH=7.50
BASEFLOW CONDITIONS: MATRIX FROM TDS
25.00 MG/L    0.00
0 0 1 0 0 0 0 0
0    0.00    0.00    0.00    0.00
     150 7.100E+01  -3.80
     460 2.700E+01  -3.90
     500 6.900E+01  -2.50
     140 2.390E+02  -5.50
     732 1.810E+02  -2.90
     180 3.500E+01  -2.80
     030 3.000E-03  -19.0
     090 5.800E-01  -5.10
     410 1.700E+01  -4.25
     580 2.000E-02  -11.0
     770 4.400E-02  -6.50
     490 2.000E-02  -6.00
     270 3.800E+00  -3.90
     231 4.000E-03  -9.00
     950 1.420E-02  -8.00
     330 0.000E-00  -7.50

  3   1
     330      7.50
```

initial charge balance is greater than 30%), solids precipitation (0 = no chemical precipitation), number of Newton-Raphson iterations (0 = 40 iterations), pH variation (0 = no pH variation), ionic strength (0 = allow MINTEQ to compute ionic strength) and numerical method (0 = Newton-Raphson iteration). Line 5 deals with what particular adsorption model will be utilized and corresponding adsorption parameters.

The next section of input (lines 6 through 22) are Type I species input lines. The first specification for each component is the corresponding MINTEQ identification number (Table 4.1). The second specification is the component's total analytical concentration (mg/l). The third specification is a guess at the log of the component's activity. To determine the dissolved Pb activity, the dissolved metal concentration from the adsorption experiment performed at pH of 7.50 was inputted, instead of the total metal concentration. At the end of this input section, a blank line must follow the last component.

The last section of input deals with what chemical species activity the user wants to have fixed (Type III). The first line of this section specified first, what type species to be considered (3) and how many species are to have their activities fixed (1). The second line specifies the component ID number (330) and the value of the fixed activity. Two blank lines must follow the last Type III species inputted in the file.

After the MINTEQ input was created, the MINTEQ program was executed and the output obtained (Table 5.6 gave the dissolved Zn activity in molar units, 6.419 E-08 moles/l). This activity concentration was a result of the MINTEQ implementation of the Davies equation, which calculates an activity coefficient that is multiplied by the dissolved Zn concentration. In addition to the dissolved metal ion activity concentration, two other output items should be observed; the charge balance computations and the saturated indices for solids.

For the charge balance computations, two values should be noted, unspeciated and speciated. These balances are computed by dividing the difference in the sum of the anions (meq/l) and the sum of the cations (meq/l) by the total sum of the anions and cations. This result is given as a percent difference. The unspeciated charge balance can give an indication that one or more ionic constituent may be missing as a Type I component if the charge balance is greater than 30%. However, the more reliable indicator is the charge balance after speciation, since chemical speciation has already been calculated. If this charge balance is greater

# TABLE 5.6 MINTEQ OUTPUT FILE

```
 MINTEQ*MINTEQ*MINTEQ*MINTEQ*MINTEQ*MINTEQ*MINTEQ*MINTEQ*MINTEQ*MINTEQ*MINTEQ*MINTEQ*MINTEQ*MINTEQ*MI

WHITE RIVER..AUGUST SAMPLING .ZINC ACTIVITY..PH=7.50
BASEFLOW CONDITIONS  MATRIX FROM TDS
T = 25.00 MG/L        0
0 0 1 0 0 0 0 0
0       0       0       0       0

     CHARGE BALANCE  UNSPECIATED

          SUM OF CATIONS= 9.208E-03 SUM OF ANIONS = 1.293E-02

          PERCENT DIFFERENCE =   -16.81   (CATIONS - ANIONS)/(ANIONS + CATIONS)

     ITERATIONS DURING SOLVE

     ITER       NAME        TOTAL MOL    DIFF FXN    LOG ACTVTY
       1   CA               1.773E-03  -1.569E-03    -3.80000
       2   CA               1.773E-03   3.581E-05    -2.86129
       3   CA               1.773E-03   6.848E-04    -2.86943
       4   CA               1.773E-03   4.828E-05    -2.99082

  OUTPUT DATA:   ITERATIONS =   4

    ID         NAME         ANAL MOL   CALC MOL   ACTIVITY    LOG ACTVTY      GAMMA      NEW LOGK    DIFF FXN
    150  CA               1.773E-03  1.525E-03 9.988E-04    -3.00054      .654898       .1838  -1.117E-06
    460  MG               1.111E-03  9.616E-04 6.343E-04    -3.19767      .659651       .1807  -6.913E-07
    500  NA               3.003E-03  2.983E-03 2.667E-03    -2.57390      .894342       .0485  -6.783E-07
    140  CO3              3.965E-03  7.524E-06 4.866E-06    -5.31279      .646774       .1892  -8.072E-07
    732  SO4              1.885E-03  1.556E-03 9.857E-04    -3.00627      .633633       .1982  -1.285E-06
    180  CL               9.879E-04  9.876E-04 8.785E-04    -3.05627      .889496       .0509  -2.479E-07
     30  AL               1.113E-07  1.776E-14 7.340E-15   -14.13433      .413280       .3838  -1.816E-11
     90  H3BO3            9.386E-06  9.197E-06 9.223E-06    -5.03514     1.002832      -.0012   7.485E-11
    410  K                4.350E-04  4.320E-04 3.842E-04    -3.41541      .889496       .0509  -1.086E-07
    580  PO4              2.107E-07  2.486E-12 9.213E-13   -12.03560      .370634       .4311  -8.363E-11
    770  H4SIO4           4.581E-07  4.562E-07 4.575E-07    -6.33964     1.002832      -.0012   5.718E-12
    490  NH4              1.109E-06  1.078E-06 9.569E-07    -6.01912      .887376       .0519  -2.829E-10
    270  F                2.001E-04  1.904E-04 1.696E-04    -3.77054      .890808       .0502  -4.769E-08
    231  CU+2             6.299E-08  1.896E-09 1.236E-09    -8.90795      .651849       .1859  -2.292E-12
    950  ZN               2.174E-07  9.848E-08 6.419E-08    -7.19252      .651849       .1859  -6.516E-11
      2  H2O                  0     -8.569E-07 9.998E-01     -.00010     1.000000       .0001       0
    330  H                    0     -4.198E-03 3.162E-08    -7.50000      .906485      7.5000       0


    SPECIES    TYPE  I - COMPONENTS

   ID         NAME          CALC MOL    ACTIVITY    LOG ACTVTY      GAMMA      NEW LOGK        DH
    150  CA                1.525E-03  9.988E-04    -3.00054      .654898        .184           0
    460  MG                9.616E-04  6.343E-04    -3.19767      .659691        .181           0
    500  NA                2.983E-03  2.667E-03    -2.57390      .894342        .048           0
    140  CO3               7.524E-06  4.866E-06    -5.31279      .646774        .189           0
    732  SO4               1.556E-03  9.857E-04    -3.00627      .633633        .198           0
    180  CL                9.876E-04  8.785E-04    -3.05627      .889496        .051           0
     30  AL                1.776E-14  7.340E-15   -14.13433      .413250        .384           0
     90  H3BO3             9.197E-06  9.223E-06    -5.03514     1.002832       -.001           0
    410  K                 4.320E-04  3.842E-04    -3.41541      .889496        .051           0
    580  PO4               2.486E-12  9.213E-13   -12.03560      .370634        .431           0
    770  H4SIO4            4.562E-07  4.575E-07    -6.33964     1.002832       -.001           0
    490  NH4               1.078E-06  9.569E-07    -6.01912      .887376        .052           0
    270  F                 1.904E-04  1.696E-04    -3.77054      .890808        .050           0
    231  CU+2              1.896E-09  1.236E-09    -8.90795      .651849        .186           0
    950  ZN                9.848E-08  6.419E-08    -7.19252      .651849        .186           0


    SPECIES    TYPE  II - COMPLEXES

    ID         NAME         CALC MOL    ACTIVITY    LOG ACTVTY      GAMMA      NEW LOGK        DH
 3305800  HPO4 -2          1.005E-07  6.462E-08    -7.18960      .643310      12.538      -3.530
 3305801  H2PO4 -          3.670E-08  3.292E-08    -7.48260      .896785      19.600      -4.520
 3300020  OH-              3.565E-07  3.176E-07    -6.49810      .890808     -13.948      13.345
 3307700  H3SIO4 -         1.910E-09  1.704E-09    -8.76843      .892447      -9.879       8.935
 3307701  H2SIO4 -2        1.710E-13  1.106E-13   -12.95625      .646774     -21.427      29.714
 7702700  SIF6 -2          2.565E-29  1.650E-29   -28.78251      .643310      30.372     -16.260
 3300900  H2BO3 -1         1.888E-07  1.675E-07    -6.77595      .887376      -9.189       3.224
  902700  BF(OH)3 -        7.034E-10  6.242E-10    -9.20468      .887376       -.347       1.850
  902701  BF2(OH)2 -       4.034E-13  3.580E-13   -12.44613      .887376       7.682       1.635
  902702  BF3OH -          2.357E-18  2.091E-18   -17.67957      .887376      13.719      -1.580
  902703  BF4 -            5.115E-23  4.539E-23   -22.34302      .887376      20.326      -1.795
 3304900  NH3 AQ           1.721E-08  1.726E-08    -7.76303     1.002832      -9.245      12.460
 4907320  NH4SO4 -         1.357E-08  1.215E-08    -7.91538      .895581       1.158           0
 4603300  MGOH +           3.663E-08  3.297E-08    -7.48188      .899955     -11.738      15.935
 4602700  MGF +            7.951E-06  7.109E-06    -5.14822      .894037       1.869       4.674
 4601400  MGCO3 AQ         2.938E-06  2.946E-06    -5.53073     1.002832       2.978       2.022
 4601401  MGHCO3 +         2.717E-05  2.425E-05    -4.61534      .892447      11.445      -2.430
 4607320  MGSO4 AQ         1.109E-04  1.112E-04    -3.95394     1.002832       2.249       1.399
 4605800  MGPO4 -          2.530E-09  2.268E-09    -8.64427      .896785       6.636       3.100
 4605801  MGH2PO4 +        7.586E-10  6.803E-10    -9.16727      .896785      21.113      -1.120
 4605802  MGHPO4 AQ        3.058E-08  3.067E-08    -7.51327     1.002832      15.219       -.230
```

(continued)

Reproduced from
best available copy.

TABLE 5.6 (continued)

```
 1503300  CAOH +        8.868E-09  7.968E-09   -8.09864    .898539   -12.552    14.535
 1501400  CAHCO3 +      3.786E-05  3.402E-05   -4.46823    .898539    11.392     1.790
 1501401  CACO3 AQ      6.887E-06  6.907E-06   -5.16072   1.002832     3.151     4.030
 1507320  CASO4 AQ      2.000E-04  2.005E-04   -3.69780   1.002832     2.308     1.470
 1505800  CAHPO4 AQ     3.529E-08  3.539E-08   -7.45114   1.002832    15.084     -.230
 1505801  CAPO4 -       2.952E-09  2.648E-09   -8.57714    .896785     6.506     3.100
 1505802  CAH2PO4 +     9.358E-10  8.392E-10   -9.07614    .896785    21.007    -1.120
 1502700  CAF +         1.647E-06  1.475E-06   -5.83108    .895581      .988     3.798
 5001400  NACO3 -       2.683E-07  2.406E-07   -6.61869    .896785     1.315     8.911
 5001401  NAHCO3 AQ     4.921E-06  4.935E-06   -5.30669   1.002832    10.079         0
 5007320  NASO4 -       1.469E-05  1.318E-05   -4.88016    .896785      .747     1.120
 5005800  NAHPO4 -      3.748E-10  3.361E-10   -9.47350    .896785    12.683         0
 5002700  NAF AQ        7.317E-08  7.338E-08   -7.13444   1.002832     -.791         0
 4107320  KSO4 -        2.968E-06  2.662E-06   -5.57486    .896785      .894     2.250
 4105800  KHPO4 -       5.449E-11  4.886E-11  -10.31101    .896785    12.687         0
  303300  ALOH +2       3.671E-12  2.374E-12  -11.62443    .646774    -4.801    11.899
  303301  AL(OH)2 +     6.498E-10  5.827E-10   -9.23453    .896785   -10.053         0
  303302  AL(OH)4 -     8.202E-08  7.333E-08   -7.13473    .894037   -22.951    44.060
  302700  ALF +2        1.970E-11  1.274E-11  -10.89488    .646774     7.199         0
  302701  ALF2 +        1.324E-09  1.187E-09   -8.92542    .896785    12.797    20.000
  302702  ALF3 AQ       3.739E-09  3.750E-09   -8.42597   1.002832    17.019     2.500
  302703  ALF4 -        3.566E-10  3.188E-10   -9.49651    .894037    19.769         0
  307320  ALSO4 +       8.473E-15  7.575E-15  -14.12060    .894037     3.069     2.150
  307321  AL(SO4)2 -    6.634E-16  5.931E-16  -15.22686    .894037     4.969     2.840
  303303  AL(OH)3 AQ    2.313E-08  2.319E-08   -7.63463   1.002832   -16.001         0
 2311400  CUCO3 AQ      3.221E-08  3.230E-08   -7.49074   1.002832     6.729         0
 2311401  CU(CO3)2-2    3.110E-10  1.979E-10   -9.70353    .636290    10.026         0
 2311800  CUCL +        3.275E-12  2.923E-12  -11.53422    .892447      .479     8.650
 2311801  CUCL2 AQ      1.375E-15  1.379E-15  -14.86049   1.002832      .159    10.560
 2311802  CUCL3 -       4.816E-21  4.298E-21  -20.36676    .892447    -2.241    13.690
 2311803  CUCL4 -2      2.941E-26  1.892E-26  -25.72303    .643310    -4.398    17.780
 2312700  CUF +         4.272E-12  3.815E-12  -11.41850    .893128     1.309     1.620
 2313300  CUOH +        4.379E-10  3.908E-10   -9.40805    .892447    -7.951         0
 2313301  CU(OH)2 AQ    2.574E-08  2.581E-08   -7.58815   1.002832   -13.681         0
 2313302  CU(OH)3 -     5.519E-14  4.929E-14  -13.30725    .893128   -26.850         0
 2313303  CU(OH)4 -2    4.875E-19  3.102E-19  -18.50835    .636290   -39.404         0
 2313304  CU2(OH)2+2    1.051E-13  6.689E-14  -13.17462    .636290   -10.162    17.539
 2317320  CUSO4 AQ      2.481E-10  2.488E-10   -9.60422   1.002832     2.309     1.220
 2311402  CUHCO3 +      2.130E-09  1.902E-09   -8.72074    .893128    13.049         0
 9501800  ZNCL +        1.701E-10  1.518E-10   -9.81879    .892447      .479     7.790
 9501801  ZNCL2 AQ      1.392E-13  1.396E-13  -12.85507   1.002832      .449     8.500
 9501802  ZNCL3 -       1.542E-16  1.376E-16  -15.86134    .892447      .549     9.560
 9501803  ZNCL4 -2      9.397E-20  6.045E-20  -19.21861    .643310      .391    10.960
 9502700  ZNF +         1.722E-10  1.538E-10   -9.81307    .893128     1.199     2.220
 9503300  ZNOH +        2.492E-09  2.225E-09   -8.65262    .893128    -8.911    13.399
 9503301  ZN(OH)2 AQ    8.073E-10  8.096E-10   -9.09172   1.002832   -16.900         0
 9503302  ZN(OH)3 -     9.063E-14  8.094E-14  -13.09182    .893128   -28.350         0
 9503303  ZN(OH)4 -2    6.374E-19  4.056E-19  -18.39192    .636290   -41.003         0
 9501804  ZNOHCL AQ     5.887E-11  5.903E-11  -10.22889   1.002832    -7.481         0
 9507320  ZNSO4 AQ      1.479E-08  1.483E-08   -7.82879   1.002832     2.369     1.360
 9507321  ZN(SO4)2-2    1.868E-10  1.188E-10   -9.92505    .636290     3.476         0
 9501400  ZNHCO3 +      2.778E-08  2.481E-08   -7.60531    .893128    12.449         0
 9501401  ZNCO3 AQ      6.215E-08  6.233E-08   -7.20531   1.002832     5.299         0
 9501402  ZN(CO3)2-2    1.019E-08  6.485E-09   -8.18810    .636290     9.826         0
 3301400  HCO3 -        3.665E-03  3.287E-03   -2.48322    .896785    10.377    -3.617
 3301401  H2CO3 AQ      2.316E-04  2.323E-04   -3.63397   1.002832    16.678    -2.247
 3307320  HSO4 -        3.384E-09  3.025E-09   -8.51920    .894037     2.036     4.910
 3302700  HF AQ         7.893E-09  7.915E-09   -8.10154   1.002832     3.168     3.460
 3302701  HF2 -         5.730E-12  5.104E-12  -11.29209    .890808     3.799     4.550
 3302702  H2F2 AQ       1.681E-16  1.686E-16  -15.77309   1.002832     6.767         0


     SPECIES:   TYPE  III - FIXED SOLIDS

    ID         NAME         CALC MOL     LOG MOL    NEW LOGK      DH
      2  H2O              -8.569E-07      -6.067       .000          0
    330  H                -4.198E-03      -2.377      7.500          0


     SPECIES:   TYPE  VI - SPECIES NOT CONSIDERED

     ID         NAME        CALC MOL     LOG MOL    NEW LOGK      DH
 3301403  CO2(GAS)        7.036E-03      -2.153     18.160      -.530
   PERCENTAGE DISTRIBUTION OF COMPONENTS


 CA
            86.1     PERCENT BOUND IN SPECIES      150    CA
             2.1     PERCENT BOUND IN SPECIES  1501400    CAHCO3 +
            11.3     PERCENT BOUND IN SPECIES  1507320    CASO4 AQ


 MG
            86.6     PERCENT BOUND IN SPECIES      460    MG
             2.4     PERCENT BOUND IN SPECIES  4601401    MGHCO3 +
            10.0     PERCENT BOUND IN SPECIES  4607320    MGSO4 AQ


 NA
            89.3     PERCENT BOUND IN SPECIES      500    NA
```

(continued)

TABLE 5.6 (continued)

```
CO3
          92.0      PERCENT BOUND IN SPECIES 3301400   HCO3 -
           5.8      PERCENT BOUND IN SPECIES 3301401   H2CO3 AQ


SO4
          82.6      PERCENT BOUND IN SPECIES     732   SO4
           5.9      PERCENT BOUND IN SPECIES 4607320   MGSO4 AQ
          10.6      PERCENT BOUND IN SPECIES 1507320   CASO4 AQ


CL
         100.0      PERCENT BOUND IN SPECIES     180   CL


AL
          73.7      PERCENT BOUND IN SPECIES  303302   AL(OH)4 -
           1.2      PERCENT BOUND IN SPECIES  302701   ALF2 +
           3.4      PERCENT BOUND IN SPECIES  302702   ALF3 AQ
          20.8      PERCENT BOUND IN SPECIES  303303   AL(OH)3 AQ


H3BO3
          98.0      PERCENT BOUND IN SPECIES      90   H3BO3
           2.0      PERCENT BOUND IN SPECIES 3300900   H2BO3 -1


K
          99.3      PERCENT BOUND IN SPECIES     410   K


PO4
          47.7      PERCENT BOUND IN SPECIES 3305800   HPO4 -2
          17.4      PERCENT BOUND IN SPECIES 3305801   H2PO4 -
           1.2      PERCENT BOUND IN SPECIES 4605800   MGPO4 -
          14.5      PERCENT BOUND IN SPECIES 4605802   MGHPO4 AQ
          16.8      PERCENT BOUND IN SPECIES 1505800   CAHPO4 AQ
           1.4      PERCENT BOUND IN SPECIES 1505801   CAPO4 -


H4SIO4
          99.6      PERCENT BOUND IN SPECIES     770   H4SIO4


NH4
          97.2      PERCENT BOUND IN SPECIES     490   NH4
           1.6      PERCENT BOUND IN SPECIES 3304900   NH3 AQ
           1.2      PERCENT BOUND IN SPECIES 4907320   NH4SO4 -


F
          95.2      PERCENT BOUND IN SPECIES     270   F
           4.0      PERCENT BOUND IN SPECIES 4602700   MGF +


CU+2
           3.0      PERCENT BOUND IN SPECIES     231   CU+2
          51.1      PERCENT BOUND IN SPECIES 2311400   CUCO3 AQ
          40.9      PERCENT BOUND IN SPECIES 2313301   CU(OH)2 AQ
           3.4      PERCENT BOUND IN SPECIES 2311402   CUHCO3 +


ZN
          45.3      PERCENT BOUND IN SPECIES     950   ZN
           1.1      PERCENT BOUND IN SPECIES 9503300   ZNOH +
           6.8      PERCENT BOUND IN SPECIES 9507320   ZNSO4 AQ
          12.8      PERCENT BOUND IN SPECIES 9501400   ZNHCO3 +
          26.6      PERCENT BOUND IN SPECIES 9501401   ZNCO3 AQ
           4.7      PERCENT BOUND IN SPECIES 9501402   ZN(CO3)2-2


H2O
          41.6      PERCENT BOUND IN SPECIES 3300020   OH-
           4.3      PERCENT BOUND IN SPECIES 4603300   MGOH +
           1.0      PERCENT BOUND IN SPECIES 1503300   CAOH +
          38.3      PERCENT BOUND IN SPECIES  303302   AL(OH)4 -
           8.1      PERCENT BOUND IN SPECIES  303303   AL(OH)3 AQ
           6.0      PERCENT BOUND IN SPECIES 2313301   CU(OH)2 AQ


H
          87.3      PERCENT BOUND IN SPECIES 3301400   HCO3 -
          11.0      PERCENT BOUND IN SPECIES 3301401   H2CO3 AQ
```

(continued)

## TABLE 5.6 (continued)

```
IDX        NAME          AQUEOUS MASS  SORBED MASS      PRECIPITATED MASS
  150   CA                 1.771E-03          0                  0
  460   MG                 1.111E-03          0                  0
  500   NA                 3.003E-03          0                  0
  140   CO3                3.984E-03          0                  0
  732   SO4                1.884E-03          0                  0
  180   CL                 9.876E-04          0                  0
   30   AL                 1.112E-07          0                  0
   90   H3BO3              9.386E-06          0                  0
  410   K                  4.349E-04          0                  0
  580   PO4                2.106E-07          0                  0
  770   H4SIO4             4.581E-07          0                  0
  490   NH4                1.109E-06          0                  0
  270   F                  2.001E-04          0                  0
  231   CU+2               6.298E-08          0                  0
  950   ZN                 2.173E-07          0                  0
    2   H2O                8.569E-07          0                  0
  330   H                  4.198E-03          0                  0

   CHARGE BALANCE. SPECIATED

        SUM OF CATIONS =  8.464E-03 SUM OF ANIONS   7.988E-03

        PERCENT DIFFERENCE =      2.89   (CATIONS - ANIONS)/(ANIONS + CATIONS)

   NONCARBONATE ALKALINITY =        0

   IONIC STRENGTH =    1.228E-02



SATURATION INDICES FOR ALL MINERALS AND SOLIDS

    ID         NAME          LOG SI      LOG K     MIN LOGK    MAX LOGK    LOG IAP        DH
 2003000 ALOH3(A)           -2.015    -10.380     -9.690           0      8.365     27.045
 6003000 ALOHSO4            -6.411      3.230      3.390       3.070     -9.641          0
 6003001 AL4(OH)10SO4       -7.245    -22.700          0           0     15.455          0
 6041000 ALUM K            -18.393      5.170          0           0    -23.563     -7.220
 6041001 ALUNITE            -5.466      1.346          0           0     -6.832     -3.918
 6015000 ANHYDRITE          -1.370      4.637          0           0     -6.007      3.769
 5015000 ARAGONITE            .023      8.336          0           0     -8.313      2.615
 5046000 ARTINITE           -6.309     -9.600          0           0      3.291     28.742
 2003001 BOEHMITE            -.213     -8.578     -8.065           0      8.365     28.130
 2046000 BRUCITE            -4.990    -16.792          0           0     11.802     25.840
 5015001 CALCITE              .162      8.475      8.560           0     -8.313      2.585
 2077000 CHALCEDONY         -2.816      3.523          0           0     -6.339     -4.615
 8646000 CHRYSOTILE         -9.460    -32.188          0           0     22.728     52.485
 8246000 CLINOENSTITE       -5.875    -11.338    -10.972     -11.632      5.463     20.015
 2077001 CRISTOBALITE       -2.752      3.587          0           0     -6.339     -5.500
 2003002 DIASPORE            1.492     -6.873          0           0      8.365     24.630
 8215000 DIOPSIDE           -8.763    -19.886          0           0     11.123     32.280
 5015002 DOLOMITE             .176     17.000          0           0    -16.824      8.290
 6046000 EPSOMITE           -4.065      2.140          0           0     -6.205     -2.820
 8646003 SEPIOLITE(C)      -11.327    -15.913          0           0      4.586     27.268
 4215000 FLUORITE             .407     10.949          0           0    -10.542     -4.710
 8046000 FORSTERITE        -11.033    -28.298          0           0     17.265     48.510
 2003003 GIBBSITE (C)        -.405     -8.770     -8.487      -9.440      8.365     22.800
 6015001 GYPSUM             -1.159      4.848          0           0     -6.007      -.261
 4150000 HALITE             -7.212     -1.582          0           0     -5.630      -.918
 5015003 HUNTITE            -3.877     29.968          0           0    -33.845     25.760
 5046001 HYDRMAGNESIT      -13.474      8.766          0           0    -22.240     52.210
 8450000 MAGADIITE         -25.151     14.300          0           0    -39.451          0
 5046002 MAGNESITE           -.481      8.029      8.279       7.779     -8.510      6.169
 6050001 MIRABILITE         -7.041      1.114          0           0     -8.155    -18.987
 3050000 NATRON             -9.151      1.311          0           0    -10.462    -15.745
 5046003 NESQUEHONITE       -2.890      5.621      5.133       4.546     -8.511      5.789
 8646001 PHLOGOPITE        -37.462    -66.300          0           0     28.838     86.360
 2077002 QUARTZ             -2.333      4.006          0           0     -6.339     -6.220
 8646004 SEPIOLITE(A)      -14.194    -18.780          0           0      4.586          0
 2077003 SIO2(A,GL)         -3.321      3.018          0           0     -6.339     -4.440
 2077004 SIO2(A,PT)         -3.629      2.710          0           0     -6.339     -3.910
 8646002 TALC              -13.006    -23.055    -18.988     -23.088     10.049     35.005
 6050002 THENARDITE         -7.975       .179          0           0     -8.154       .572
 5050001 THERMONATR        -10.586      -.125          0           0    -10.461      2.802
 8215001 TREMOLITE         -24.252    -56.546          0           0     32.294     96.615
 4123100 MELANOTHALLI      -18.750     -3.730          0      -4.450    -15.020     12.320
 5023100 CUCO3              -4.591      9.630      9.650       9.610    -14.221          0
 4223100 CUF2              -15.829       .620          0           0    -16.449     13.320
 4223101 CUF2, 2H2O        -11.899      4.550          0           0    -16.449      3.650
 2023100 CU(OH)2            -2.548     -8.640          0      -9.200      6.092     15.250
 4123101 ATACAMITE          -5.712     -7.340     -7.240      -7.490      1.628     18.690
 6023100 ANTLERITE          -8.021     -8.290          0      -8.900       .269          0
 6023101 BROCHANTITE        -8.979    -15.340    -15.150     -15.500      6.361          0
 6023102 LANGITE           -10.429    -16.790          0     -17.400      6.361     39.610
 2023101 TENORITE           -1.528     -7.620     -7.350      -7.890      6.092     15.240
 6023103 CUOCUSO4          -17.352    -11.530          0           0     -5.822     35.575
 7023100 CU3(PO4)2         -13.945     36.850          0      36.900    -50.795          0
 7023101 CU3(PO4)2,3W      -15.675     35.120          0           0    -50.795          0
 6023104 CUSO4             -14.924     -3.010     -2.630      -3.420    -11.914     18.140
 6023105 CHALCANTHITE       -9.275      2.640      2.960       2.135    -11.915     -1.440
 2023102 DIOPTASE           -6.748     -6.500          0           0      -.248      8.960
 4195000 ZNCL2             -20.335     -7.030          0      -7.060    -13.305     17.480
 5095000 SMITHSONITE        -2.505     10.000     10.810       9.820    -12.505      4.360
```

(continued)

## TABLE 5.6 (continued)

```
5095001 ZNCO3, 1H2O        -2.245     10.260          0          0    -12.505          0
4295000 ZNF2              -13.214      1.520          0      1.080    -14.734     13.080
2095000 ZN(OH)2 (A)        -4.643    -12.450    -12.260    -12.480      7.807          0
2095001 ZN(OH)2 (C)        -4.393    -12.200          0          0      7.807          0
2095002 ZN(OH)2 (B)        -3.943    -11.750    -11.320    -11.890      7.807          0
2095003 ZN(OH)2 (G)        -3.903    -11.710    -11.190    -11.840      7.807          0
2095004 ZN(OH)2 (E)        -3.693    -11.500    -10.950    -11.620      7.807          0
4195001 ZN2(OH)3CL        -10.142    -15.200          0          0      5.056          0
4195002 ZN5(OH)8CL2       -20.576    -38.500          0          0     17.924          0
6095000 ZN2(OH)2SO4        -9.892     -7.500          0          0     -2.392          0
6095001 ZN4(OH)6SO4       -15.177    -28.400          0          0     13.223          0
2095005 ZNO(ACTIVE)        -3.503    -11.310    -11.570    -11.860      7.807          0
2095006 ZINCITE            -3.333    -11.140    -10.990    -11.540      7.807     21.860
6095002 ZN3O(SO4)2        -31.610    -19.020          0          0    -12.590     62.000
7095000 ZN3(PO4),4W       -13.609     32.040          0          0    -45.649          0
8295000 ZNSIO3             -1.462     -2.930          0          0      1.468     18.270
8095000 WILLEMITE          -6.055    -15.330    -13.350          0      9.275     33.370
6095003 ZINCOSITE         -13.209     -3.010          0     -3.930    -10.199     19.200
6095004 ZNSO4, 1H2O        -9.629       .570          0       .500    -10.199     10.640
6095005 BIANCHITE          -8.434      1.765          0      1.020    -10.199       .160
6095006 GOSLARITE          -8.239      1.960          0      1.870    -10.199     -3.300
8450001 ANALCIME           -6.106     -6.719          0          0       .613     22.840
8603000 HALLOYSITE         -4.942     -8.994          0          0      4.052     39.730
8603001 KAOLINITE          -1.674     -5.726          0          0      4.052     35.280
8415000 LEONHARDITE        -9.745    -16.490          0          0      6.745     85.360
8450002 LOW ALBITE         -8.319     -2.592          0          0     -5.727     17.400
8450003 ANALBITE           -9.233     -3.506          0          0     -5.727     20.000
8641000 MUSCOVITE          -2.827    -12.990          0          0     10.163     59.340
8415001 ANORTHITE          -9.378    -25.430          0          0     16.052     70.660
8603002 PYROPHYLLITE       -7.029      1.598          0          0     -8.627          0
8415002 LAUMONTITE        -11.088    -14.460          0          0      3.372     50.450
8415003 WAIRAKITE         -15.498    -18.870          0          0      3.372     63.150
5023101 MALACHITE          -2.949      5.180          0      3.940     -8.129     15.610
5023102 AZURITE            -5.430     16.920          0          0    -22.350     23.770
5295000 ZN(BO2)2          -10.553     -8.290          0          0     -2.203          0
2015000 LIME              -20.798    -32.797          0          0     11.999     46.265
2015001 PORTLANDITE       -10.676    -22.675          0          0     11.999     30.690
2046001 PERICLASE          -9.708    -21.510          0          0     11.802     36.135
3046000 SPINEL             -7.800    -36.333          0          0     28.533     89.089
4250000 CRYOLITE          -12.989     31.490          0          0    -44.479    -10.904
8215002 WOLLASTONITE       -7.336    -12.996          0          0      5.660     19.498
8215003 P-WOLLSTANIT       -8.186    -13.846          0          0      5.660     21.068
8015001 CA-OLIVINE        -19.990    -37.649          0          0     17.659     54.695
8015002 LARNITE           -21.482    -39.141          0          0     17.659     57.238
8015007 CA3SIO5           -44.208    -73.867          0          0     29.659    106.335
8015003 MONTICELLITE      -12.810    -30.272          0          0     17.462     49.421
8015005 AKERMINITE        -24.350    -47.472          0          0     23.122     76.445
8015004 MERWINITE         -33.422    -68.543          0          0     35.121    107.111
8441000 KALSILITE          -6.727    -12.838          0          0      6.111     28.919
8441001 LEUCITE            -6.652     -6.423          0          0      -.229     22.065
8441002 MICROCLINE         -7.184      -.616          0          0     -6.568     12.309
8441003 H SANIDINE         -7.630     -1.062          0          0     -6.568     14.252
8450004 NEPHELINE          -7.266    -14.218          0          0      6.952     33.204
8015006 GEHLENITE         -22.432    -56.822          0          0     34.390    116.125
                   NORMAL TERMINATION OF MINTEQ
```

than 20%, then it is very likely an ionic component is absent. If environmental data are lacking, an ion concentration adjustment may be required on a conservative Type I component.

To obtain an indication of what solids will precipitate for the full MINTEQ model run, in the output section headed by Saturation Indices for all Minerals and Solids, the log SI column should be observed. From Table 5.6, the SI values for diaspore, argonite, calcite and fluorite all have positive indices, indicating the solid is oversaturated in the system. However, due to kinetic factors, the solids may not actually obtain equilibrium in the time frame considered, or may not actually form due to the constraints placed on the system, such as no fixed partial pressure (open to atmosphere). Some of these solids form under high partial pressures of $CO_2$ (groundwater environment) and if used in a system with no fixed partial pressure, a Gibbs Phase Rule Violation will occur. General guidelines for selecting solid phases are given in the MINTEQ Technical Manual.

To determine which MINTEQ adsorption model can be implemented to model the system, data obtained from the metal addition reactor studies and MINTEQ were plotted. The first approach was to plot particulate metal concentration (moles/l) versus dissolved metal ion activity concentration (moles/l) obtained for various total metal concentrations for a specific pH from MINTEQ. From Figure 5.8 it can be seen that a linear relationship developed for the metal Zn at pH 8.39 (ambient pH). A linear regression was performed and the slope of the line (activity Kd) was determined to be 3.53 E+02. The log value of the Kd was then utilized as an input parameter when implementing the MINTEQ adsorption model.

## 5.6 ACTIVITY Kd MODELING WITH MINTEQ

In utilizing the activity Kd approach to model metal-sediment adsorption, a new MINTEQ input file had to be developed (Table 5.7). This file was created by modifications and additions to an existing activity MINTEQ input file. The first modification was to line 4, where the number of Newton-Raphson iterations was increased from 40 to 100. The second modification occurred on line 5, where the first specification was changed to 1, designating the activity Kd adsorption routine. In the Type I component input section, the dissolved metal concentration for Zn is replaced by the total metal concentration (.524 mg/l). The component for surface sites (ID 990) was then added as a Type I component and its activity fixed as a Type III species.

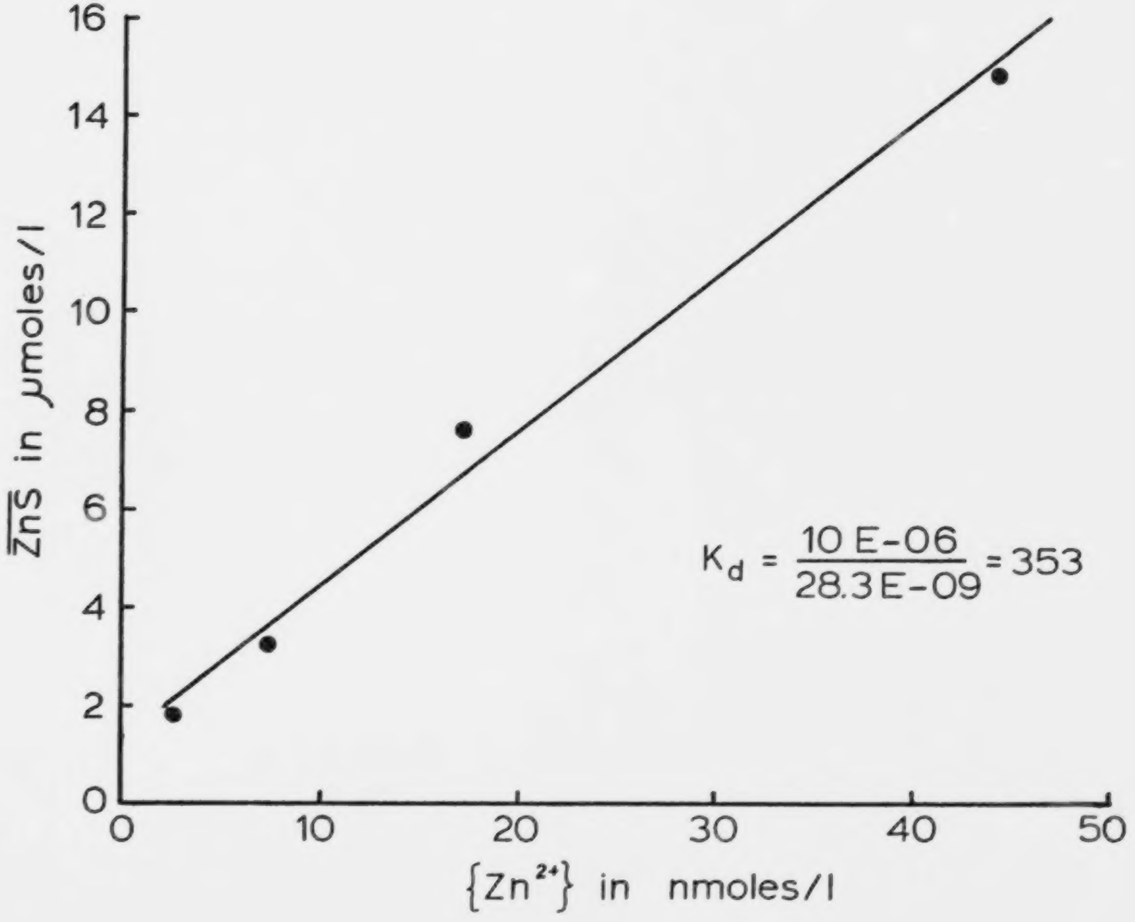


Figure 5.8 Zn ion activity vs. particulate Zn, pH = 8.4.

## TABLE 5.7 MINTEQ ZINC ADSORPTION INPUT FILE

```
WHITE RIVER APRIL SAMPLING..LOG KD=2.51..PH=8.39..TSS=.551G L-1
BASEFLOW RUNOFF CONDITIONS; MATRIX FROM TDS..TOTAL METAL=524(PPB-ZN)
25.00 MG/L    0.00
0 0 0 0 2 0 0 0
1    0.00    0.00    0.00    0.00
     150 7.100E+01  -3.80
     460 2.700E+01  -3.90
     500 6.900E+01  -2.50
     140 2.390E+02  -5.50
     732 1.810E+02  -2.90
     180 3.500E+01  -2.80
     030 3.000E-03  -19.0
     090 5.800E-01  -5.10
     410 1.700E+01  -4.25
     580 2.000E-02  -11.0
     770 4.400E-02  -6.50
     490 2.000E-02  -6.00
     270 3.800E+00  -3.90
     231 4.000E-02  -9.00
     950 5.240E-01  -8.00
     990 0.000E-00   0.00
     330 0.000E-00  -8.39

  3   2
     330      8.39
     990
  5   4
5015001
2003002
5015002
2023101

  2   1
9909501 SOH-ZN                          2.51
      2    1.00 950    1.00 990
```

The first addition to the activity MINTEQ file involved inserting four Type V species. These species (calcite, dolomite, diaspore, tenorite) are allowed to precipitate in the system if their saturation indices are exceeded during chemical speciation. The last addition involved a Type II modification (insertion of species not in data base) to incorporate the adsorption "reaction" between Zn and the surface sites (SOH). These lines contain the necessary data for the new species: ID number, name, log Kd, number of components in reaction, stoichiometry and ID number of components involved in the adsorption reaction. It is also possible to simultaneously run two or three adsorption reactions with different metals, since there is a large excess of surface sites relative to available metal. Competition for available surface sites is not considered. These new MINTEQ files were developed and executed for all Zn reactor experiments involving four total metal levels (.124 mg/l, .224 mg/l, .524 mg/l, and 1.024 mg/l) at two specific pH conditions that conformed to the activity Kd approach (pH 7.50 and 8.39).

The MINTEQ output data is divided into seven sections. The first section is a duplication of the first five lines of the MINTEQ input file (Table 5.8). Section II provides the initial charge balance of the system being modeled prior to chemical speciation. This section also gives the number of the Newton-Raphson convergence iterations required to obtain the real component activity in comparison to the initial guess. Section III presents six types of information for all Type I species inputed: the analytical molarity, calculated molarity, activity, activity coefficient (GAMMA), new log K (corrected equilibrium constant for temperature and ionic strength) and DIFF FXN (difference between the analytical total and the sum of all aqueous and adsorbed species calculated by the model). It should be noted that $H_2O$ is always considered a Type I species and is added as a Type I and III species by MINTEQ. Section IV provides thermodynamic data for all six types of species considered by MINTEQ for speciation calculations. The output for Type I and Type II species are similar, with the following information presented: calculated molarity, activity, log activity, activity coefficient (GAMMA), new log K and the enthalpy of reaction (DH). Information for Type III, IV and V species includes: calculated molarity, log molarity, new log K and enthalpy of reaction. Section V lists the percent distribution of the components, in which all species printed contribute to one percent or greater to the total analytical mass. For example, 97.5% of the total analytical mass inputed for Zn was bounded to the sediment surface sites and 1% was in the form of $ZnCO_3$. Section VI output reflects the total aqueous, sorbed and precipitated masses for each Type I species in moles per liter. The final output section provides the following information for Type IV species: saturation index, log K,

# TABLE 5. 8 MINTEQ ZINC ADSORPTION OUTPUT FILE

```
  MINTEQ*MINTEQ*MINTEQ*MINTEQ*MINTEQ*MINTEQ*MINTEQ*MINTEQ*MINTEQ*MINTEQ*MINTEQ*MINTEQ*MINTEQ*MINTEQ*MINTEQ*

WHITE RIVER APRIL SAMPLING..LOG KD=2.51..PH=8.39..TSS= 551G L-1
BASEFLOW RUNOFF CONDITIONS; MATRIX FROM TDS .TOTAL METAL=524(PPB-ZN)
T = 25.00 MG/L       0
0 0 0 0 2 0 0 0
1      0      0      0      0

     CHARGE BALANCE: UNSPECIATED

          SUM OF CATIONS= 9.225E-03 SUM OF ANIONS = 1.293E-02

          PERCENT DIFFERENCE =    -16.72   (CATIONS - ANIONS)/(ANIONS + CATIONS)

     ITERATIONS DURING SOLVE

     ITER       NAME          TOTAL MOL    DIFF FXN     LOG ACTVTY
       1    CA                 1.773E-03  -1.572E-03     -3.80000
       2    CA                 1.773E-03   1.296E-04     -2.85760
       3    CA                 1.773E-03   6.561E-04     -2.86779
       4    CA                 1.773E-03   4.698E-05     -3.00279

   OUTPUT DATA:   ITERATIONS =   4

    ID         NAME          ANAL MOL    CALC MOL   ACTIVITY    LOG ACTVTY      GAMMA       NEW LOGK    DIFF FXN
    150   CA               1.773E-03  1.484E-03 9.713E-04    -3.01265      .654528        .1841  -9.699E-07
    460   MG               1.111E-03  9.434E-04 6.220E-04    -3.20622      .659331        .1809  -6.065E-07
    500   NA               3.003E-03  2.981E-03 2.665E-03    -2.57425      .894201        .0486  -6.176E-07
    140   CO3              3.985E-03  5.971E-05 3.860E-05    -4.41343      .646385        .1895  -7.858E-07
    732   SO4              1.885E-03  1.562E-03 9.892E-04    -3.00470      .633215        .1964  -1.159E-06
    180   CL               9.879E-04  9.876E-04 8.783E-04    -3.05634      .889341        .0509  -2.259E-07
     30   AL               1.113E-07  6.406E-18 2.645E-18   -17.57763      .412825        .3842  -2.243E-11
     90   H3BO3            9.386E-06  8.095E-06 8.118E-06    -5.09054     1.002842      -.0012  -2.077E-10
    410   K                4.350E-04  4.320E-04 3.842E-04    -3.41549      .889341        .0509  -9.894E-08
    580   PO4              2.107E-07  1.922E-11 7.113E-12   -11.14792      .370120        .4317  -9.235E-11
    770   H4SIO4           4.581E-07  4.436E-07 4.449E-07    -6.35173     1.002842      -.0012   2.355E-12
    490   NH4              1.109E-06  9.760E-07 8.659E-07    -6.06251      .887215        .0520  -2.319E-10
    270   F                2.001E-04  1.906E-04 1.698E-04    -3.77012      .890657        .0503  -4.333E-08
    231   CU+2             6.299E-07  6.517E-10 4.246E-10    -9.37207      .651470        .1861   7.532E-13
    950   ZN               8.021E-06  3.573E-08 2.328E-08    -7.63303      .651470        .1861  -2.175E-10
      2   H2O                  0     -4.664E-06 9.998E-01     -.00010     1.000000        .0001      0
    330   H                    0     -3.871E-03 4.074E-09    -8.39000      .906374       8.3900      0
    990   SOH1                 0     -7.533E-06 1.000E+00         0       1.000000           0       0


    SPECIES:    TYPE  I - COMPONENTS

   ID         NAME          CALC MOL    ACTIVITY    LOG ACTVTY      GAMMA     NEW LOGK        DH
    150   CA               1.484E-03   9.713E-04    -3.01265      .654528       .184           0
    460   MG               9.434E-04   6.220E-04    -3.20622      .659331       .181           0
    500   NA               2.981E-03   2.665E-03    -2.57425      .894201       .049           0
    140   CO3              5.971E-05   3.860E-05    -4.41343      .646385       .190           0
    732   SO4              1.562E-03   9.892E-04    -3.00470      .633215       .198           0
    180   CL               9.876E-04   8.783E-04    -3.05634      .889341       .051           0
     30   AL               6.406E-18   2.645E-18   -17.57763      .412825       .384           0
     90   H3BO3            8.095E-06   8.118E-06    -5.09054     1.002842      -.001           0
    410   K                4.320E-04   3.842E-04    -3.41549      .889341       .051           0
    580   PO4              1.922E-11   7.113E-12   -11.14792      .370120       .432           0
    770   H4SIO4           4.436E-07   4.449E-07    -6.35173     1.002842      -.001           0
    490   NH4              9.760E-07   8.659E-07    -6.06251      .887215       .052           0
    270   F                1.906E-04   1.698E-04    -3.77012      .890657       .050           0
    231   CU+2             6.517E-10   4.246E-10    -9.37207      .651470       .186           0
    950   ZN               3.573E-08   2.328E-08    -7.63303      .651470       .186           0


    SPECIES:    TYPE  II - COMPLEXES

    ID         NAME          CALC MOL    ACTIVITY    LOG ACTVTY      GAMMA     NEW LOGK        DH
9909501   SOH-ZN           7.533E-06   7.533E-06    -5.12303     1.000000      2.510           0
3305800   HPO4 -2          9.998E-08   6.428E-08    -7.19192      .642913     12.538      -3.530
3305801   H2PO4 -          4.704E-09   4.218E-09    -8.37492      .896650     19.600      -4.520
3300020   OH-              2.768E-06   2.465E-06    -5.60810      .890657    -13.948      13.345
3307700   H3SIO4 -         1.442E-08   1.287E-08    -7.89051      .892300     -9.879       8.935
3307701   H2SIO4 -2        1.003E-11   6.481E-12   -11.18834      .646385    -21.427      29.714
7702700   SIF6 -2          6.915E-33   4.446E-33   -32.35208      .642913     30.372     -16.260
3300900   H2BO3 -1         1.290E-06   1.145E-06    -5.94135      .887215     -9.189       3.224
 902700   BF(OH)3 -        6.199E-10   5.500E-10    -9.25966      .887215      -.347       1.850
 902701   BF2(OH)2 -       4.584E-14   4.067E-14   -13.39069      .887215      7.682       1.635
 902702   BF3OH -          3.453E-20   3.064E-20   -19.51371      .887215     13.719      -1.580
 902703   BF4 -            9.666E-26   8.576E-26   -25.06674      .887215     20.326      -1.795
3304900   NH3 AQ           1.209E-07   1.212E-07    -6.91643     1.002842     -9.245      12.480
4907320   NH4SO4 -         1.232E-08   1.104E-08    -7.95721      .895443      1.158           0
```

Reproduced from
best available copy.

## TABLE 5.8 (continued)

```
4603300  MGOH +        2.789E-07  2.509E-07   -6.60043    .899828   -11.738   15.935
4602700  MGF +         7.805E-06  6.977E-06   -5.15634    .893895     1.869    4.674
4601400  MGCO3 AQ      2.285E-05  2.291E-05   -4.63992   1.002842     2.978    2.022
4601401  MGHCO3 +      2.722E-05  2.429E-05   -4.61452    .892300    11.445   -2.430
4607320  MGSO4 AQ      1.091E-04  1.094E-04   -3.96092   1.002842     2.249    1.399
4605800  MGPO4 -       1.915E-08  1.717E-08   -7.76514    .896650     6.636    3.100
4605801  MGH2PO4 +     9.533E-11  8.548E-11  -10.06814    .896650    21.113   -1.120
4605802  MGHPO4 AQ     2.983E-08  2.991E-08   -7.52414   1.002842    15.219    -.230
1503300  CAOH +        6.695E-08  6.015E-08   -7.22075    .898408   -12.551   14.535
1501400  CAHCO3 +      3.763E-05  3.381E-05   -4.47098    .898408    11.392    1.790
1501401  CACO3 AQ      5.313E-05  5.328E-05   -4.27346   1.002842     3.151    4.030
1507320  CASO4 AQ      1.952E-04  1.957E-04   -3.70835   1.002842     2.308    1.470
1505800  CAHPO4 AQ     3.413E-08  3.423E-08   -7.46557   1.002842    15.084    -.230
1505801  CAPO4 -       2.217E-08  1.988E-08   -7.70157    .896650     6.506    3.100
1505802  CAH2PO4 +     1.166E-10  1.046E-10   -9.98057    .896650    21.007   -1.120
1502700  CAF +         1.604E-06  1.436E-06   -5.84277    .895443      .988    3.798
5001400  NACO3 -       2.127E-06  1.907E-06   -5.71967    .896650     1.315    8.911
5001401  NAHCO3 AQ     5.025E-06  5.039E-06   -5.29767   1.002842    10.079        0
5007320  NASO4 -       1.474E-05  1.321E-05   -4.87895    .896650      .747    1.120
5005800  NAHPO4 -      3.726E-10  3.341E-10   -9.47617    .896650    12.683        0
5002700  NAF AQ        7.318E-08  7.339E-08   -7.13437   1.002842     -.791        0
4107320  KSO4 -        2.979E-06  2.671E-06   -5.57337    .896650      .894    2.250
4105800  KHPO4 -       5.420E-11  4.860E-11  -10.31341    .896650    12.687        0
 303300  ALOH +2       1.028E-14  6.642E-15  -14.17773    .646385    -4.800   11.899
 303301  AL(OH)2 +     1.411E-11  1.265E-11  -10.89783    .896650   -10.053        0
 303302  AL(OH)4 -     1.073E-07  9.593E-08   -7.01802    .893895   -22.951   44.060
 302700  ALF +2        7.108E-15  4.595E-15  -14.33775    .646385     7.200        0
 302701  ALF2 +        4.781E-13  4.287E-13  -12.36788    .896650    12.797   20.000
 302702  ALF3 AQ       1.351E-12  1.355E-12  -11.86800   1.002842    17.019    2.500
 302703  ALF4 -        1.290E-13  1.153E-13  -12.93812    .893895    19.769        0
 307320  ALSO4 +       3.065E-18  2.740E-18  -17.56233    .893895     3.069    2.150
 307321  AL(SO4)2 -    2.408E-19  2.153E-19  -18.66703    .893895     4.969    2.840
 303303  AL(OH)3 AQ    3.898E-09  3.909E-09   -8.40792   1.002842   -16.001        0
2311400  CUCO3 AQ      8.776E-08  8.801E-08   -7.05549   1.002842     6.729        0
2311401  CU(CO3)2-2    6.725E-09  4.276E-09   -8.36892    .635882    10.027        0
2311800  CUCL +        1.125E-12  1.004E-12  -11.99840    .892300      .479    8.650
2311801  CUCL2 AQ      4.721E-16  4.734E-16  -15.32474   1.002842      .159   10.560
2311802  CUCL3 -       1.654E-21  1.475E-21  -20.83107    .892300    -2.241   13.690
2311803  CUCL4 -2      1.010E-26  6.495E-27  -26.18741    .642913    -4.398   17.780
2312700  CUF +         1.469E-12  1.312E-12  -11.88219    .892985     1.309    1.620
2313300  CUOH +        1.168E-09  1.042E-09   -8.98217    .892300    -7.951        0
2313301  CU(OH)2 AQ    5.327E-07  5.342E-07   -6.27226   1.002842   -13.681        0
2313302  CU(OH)3 -     8.867E-12  7.916E-12  -11.10136    .892985   -26.850        0
2313303  CU(OH)4 -2    6.084E-16  3.868E-16  -15.41246    .635882   -39.403        0
2313304  CU2(OH)2+2    7.478E-13  4.755E-13  -12.32284    .635882   -10.162   17.539
2317320  CUSO4 AQ      8.551E-11  8.575E-11  -10.06677   1.002842     2.309    1.220
2311402  CUHCO3 +      7.476E-10  6.676E-10   -9.17549    .892985    13.049        0
9501800  ZNCL +        6.168E-11  5.503E-11  -10.25937    .892300      .479    7.790
9501801  ZNCL2 AQ      5.047E-14  5.062E-14  -13.29571   1.002842      .449    8.500
9501802  ZNCL3 -       5.590E-17  4.988E-17  -16.30204    .892300      .549    9.560
9501803  ZNCL4 -2      3.408E-20  2.191E-20  -19.65938    .642913      .391   10.960
9502700  ZNF +         6.252E-11  5.583E-11  -10.25316    .892985     1.199    2.220
9503300  ZNOH +        7.015E-09  6.264E-09   -8.20313    .892985    -8.811   13.399
9503301  ZN(OH)2 AQ    1.764E-08  1.769E-08   -7.75223   1.002842   -16.900        0
9503302  ZN(OH)3 -     1.538E-11  1.373E-11  -10.86233    .892985   -28.350        0
9503303  ZN(OH)4 -2    8.398E-16  5.340E-16  -15.27243    .635882   -41.002        0
9501804  ZNOHCL AQ     1.657E-10  1.662E-10   -9.77947   1.002842    -7.481        0
9507320  ZNSO4 AQ      5.383E-09  5.398E-09   -8.26773   1.002842     2.369    1.360
9507321  ZN(SO4)2-2    6.826E-11  4.341E-11  -10.36243    .635882     3.477        0
9501400  ZNHCO3 +      1.030E-08  9.195E-09   -8.03646    .892985    12.449        0
9501401  ZNCO3 AQ      1.788E-07  1.793E-07   -6.74646   1.002842     5.299        0
9501402  ZN(CO3)2-2    2.327E-07  1.480E-07   -6.82988    .635882     9.827        0
3301400  HCO3 -        3.746E-03  3.358E-03   -2.47386    .896650    10.377   -3.617
3301401  H2CO3 AQ      3.049E-05  3.058E-05   -4.51461   1.002842    16.678   -2.247
3307320  HSO4 -        4.376E-10  3.912E-10   -9.40764    .893895     2.036    4.910
3302700  HF AQ         1.018E-09  1.021E-09   -8.99112   1.002842     3.168    3.460
3302701  HF2 -         7.397E-13  6.588E-13  -12.18125    .890657     3.799    4.550
3302702  H2F2 AQ       2.796E-18  2.804E-18  -17.55225   1.002842     6.767        0


SPECIES:   TYPE  III - FIXED SOLIDS

 ID          NAME         CALC MOL     LOG MOL    NEW LOGK      DH
   2   H2O              -4.664E-06      -5.331       .000         0
 330   H                -3.871E-03      -2.412      8.390         0
 990   SOH1             -7.533E-06      -5.123          0         0


SPECIES:   TYPE  V - DISSOLVED SOLIDS

   ID          NAME        CALC MOL     LOG MOL    NEW LOGK      DH
2003002  DIASPORE         5.238E-00       .719     -6.873     24.630
5015002  DOLOMITE         9.001E-01      1.954     17.000      8.290
2023101  TENORITE         6.135E-01      -.212     -7.620     15.240
5015001  CALCITE          1.119E-01      1.049      8.475      2.585


SPECIES:   TYPE  VI - SPECIES NOT CONSIDERED

   ID          NAME        CALC MOL     LOG MOL    NEW LOGK      DH
3301403  CO2(GAS)         9.261E-04     -3.033     18.160      -.830
```

(continued)

# TABLE 5.8 (continued)

```
PERCENTAGE DISTRIBUTION OF COMPONENTS


CA
          83.8      PERCENT BOUND IN SPECIES     150   CA
           2.1      PERCENT BOUND IN SPECIES 1501400   CAHCO3 +
           3.0      PERCENT BOUND IN SPECIES 1501401   CACO3 AQ
          11.0      PERCENT BOUND IN SPECIES 1507320   CASO4 AQ


MG
          84.9      PERCENT BOUND IN SPECIES     460   MG
           2.1      PERCENT BOUND IN SPECIES 4601400   MGCO3 AQ
           2.5      PERCENT BOUND IN SPECIES 4601401   MGHCO3 +
           9.8      PERCENT BOUND IN SPECIES 4607320   MGSO4 AQ


NA
          99.3      PERCENT BOUND IN SPECIES     500   NA


CO3
           1.5      PERCENT BOUND IN SPECIES     140   CO3
           1.3      PERCENT BOUND IN SPECIES 1501401   CACO3 AQ
          94.0      PERCENT BOUND IN SPECIES 3301400   HCO3 -


SO4
          82.9      PERCENT BOUND IN SPECIES     732   SO4
           5.8      PERCENT BOUND IN SPECIES 4607320   MGSO4 AQ
          10.4      PERCENT BOUND IN SPECIES 1507320   CASO4 AQ


CL
         100.0      PERCENT BOUND IN SPECIES     180   CL


AL
          96.5      PERCENT BOUND IN SPECIES  303302   AL(OH)4 -
           3.5      PERCENT BOUND IN SPECIES  303303   AL(OH)3 AQ


H3BO3
          86.2      PERCENT BOUND IN SPECIES      90   H3BO3
          13.7      PERCENT BOUND IN SPECIES 3300900   H2BO3 -1


K
          99.3      PERCENT BOUND IN SPECIES     410   K


PO4
          47.5      PERCENT BOUND IN SPECIES 3305800   HPO4 -2
           2.2      PERCENT BOUND IN SPECIES 3305801   H2PO4 -
           9.1      PERCENT BOUND IN SPECIES 4605800   MGPO4 -
          14.2      PERCENT BOUND IN SPECIES 4605802   MGHPO4 AQ
          16.2      PERCENT BOUND IN SPECIES 1505800   CAHPO4 AQ
          10.5      PERCENT BOUND IN SPECIES 1505801   CAPO4 -

H4SIO4
          96.8      PERCENT BOUND IN SPECIES     770   H4SIO4
           3.1      PERCENT BOUND IN SPECIES 3307700   H3SIO4 -


NH4
          88.0      PERCENT BOUND IN SPECIES     490   NH4
          10.9      PERCENT BOUND IN SPECIES 3304900   NH3 AQ
           1.1      PERCENT BOUND IN SPECIES 4907320   NH4SO4 -


F
          95.3      PERCENT BOUND IN SPECIES     270   F
           3.9      PERCENT BOUND IN SPECIES 4602700   MGF +


CU+2
          13.9      PERCENT BOUND IN SPECIES 2311400   CUCO3 AQ
           1.1      PERCENT BOUND IN SPECIES 2311401   CU(CO3)2-2
          84.6      PERCENT BOUND IN SPECIES 2313301   CU(OH)2 AQ
```

(continued)

## TABLE 5. 8 (continued)

```
ZN
        93.9      PERCENT BOUND IN SPECIES 9909501   SOH-ZN
         2.2      PERCENT BOUND IN SPECIES 9501401   ZNCO3 AQ
         2.9      PERCENT BOUND IN SPECIES 9501402   ZN(CO3)2-2


H2O
        59.3      PERCENT BOUND IN SPECIES 3300020   OH-
         6.0      PERCENT BOUND IN SPECIES 4603300   MGOH +
         1.4      PERCENT BOUND IN SPECIES 1503300   CAOH +
         9.2      PERCENT BOUND IN SPECIES  303302   AL(OH)4 -
        22.8      PERCENT BOUND IN SPECIES 2313301   CU(OH)2 AQ


H
        96.8      PERCENT BOUND IN SPECIES 3301400   HCO3 -
         1.6      PERCENT BOUND IN SPECIES 3301401   H2CO3 AQ


SOH1
       100.0      PERCENT BOUND IN SPECIES 9909501   SOH-ZN

  IDX        NAME        AQUEOUS MASS  SORBED MASS      PRECIPITATED MASS
    150  CA                1.772E-03           0                   0
    460  MG                1.111E-03           0                   0
    500  NA                3.003E-03           0                   0
    140  CO3               3.984E-03           0                   0
    732  SO4               1.884E-03           0                   0
    180  CL                9.876E-04           0                   0
     30  AL                1.112E-07           0                   0
     90  H3BO3             9.386E-06           0                   0
    410  K                 4.349E-04           0                   0
    580  PO4               2.106E-07           0                   0
    770  H4SIO4            4.581E-07           0                   0
    490  NH4               1.109E-06           0                   0
    270  F                 2.001E-04           0                   0
    231  CU+2              6.299E-07           0                   0
    950  ZN                4.879E-07     7.533E-06                 0
      2  H2O               4.664E-06           0                   0
    330  H                 3.871E-03           0                   0

    CHARGE BALANCE: SPECIATED

         SUM OF CATIONS =  8.343E-03 SUM OF ANIONS   8.192E-03

         PERCENT DIFFERENCE =       .91   (CATIONS - ANIONS)/(ANIONS + CATIONS)

    NONCARBONATE ALKALINITY =       0

    IONIC STRENGTH =    1.232E-02
```

```
ITERATIONS=   4:  SOLID CALCITE       PRECIPITATES
     5    CA              -2.213E-03   3.070E-03     -3.01265
     6    CA              -2.213E-03  -1.064E-03     -4.01265
     7    CA              -2.213E-03  -2.364E-04     -3.90127
     8    CA              -2.213E-03  -1.557E-05     -3.86702

ITERATIONS=   8:  SOLID DOLOMITE      PRECIPITATES
     9    CA              -1.101E-03  -7.648E-04     -3.86452
    10    CA              -1.101E-03  -1.602E-04     -3.75259
    11    CA              -1.101E-03  -1.316E-05     -3.71938

ITERATIONS=  11:  SOLID DIASPORE      PRECIPITATES
    12    NA               3.003E-03  -2.625E-04     -2.56531
    13    CA              -1.101E-03  -5.404E-06     -3.72427
    14    NA               3.003E-03   7.980E-06     -2.56419

OUTPUT DATA:  ITERATIONS =  14

 ID          NAME         ANAL MOL   CALC MOL   ACTIVITY    LOG ACTVTY       GAMMA       NEW LOGK    DIFF FXN
  150  CA                1.773E-03  2.726E-04 1.920E-04     -3.71678      .704245        .1523   9.281E-09
  231  CU+2              6.299E-07  6.606E-10 4.639E-10     -9.33359      .702165        .1536  -1.162E-12
  500  NA                3.003E-03  2.982E-03 2.721E-03     -2.56532      .912428        .0398   1.966E-07
  950  ZN                8.021E-06  3.442E-08 2.417E-08     -7.61681      .702165        .1536   2.115E-11
  732  SO4               1.885E-03  1.779E-03 1.225E-03     -2.91171      .688888        .1619   4.839E-07
  180  CL                9.879E-04  9.879E-04 8.982E-04     -3.04662      .909190        .0413   6.992E-08
  270  F                 2.001E-04  1.975E-04 1.798E-04     -3.74530      .910088        .0409   1.386E-08
   90  H3BO3             9.386E-06  8.122E-06 8.136E-06     -5.08957     1.001794       -.0008   6.889E-11
  410  K                 4.350E-04  4.314E-04 3.922E-04     -3.40649      .909190        .0413   3.087E-08
  580  PO4               2.107E-07  2.781E-11 1.230E-11    -10.91013      .442322        .3543   4.235E-11
  770  H4SIO4            4.581E-07  4.440E-07 4.447E-07     -6.35189     1.001794       -.0008  -3.337E-13
  490  NH4               1.109E-06  9.711E-07 8.815E-07     -6.05476      .907773        .0420   7.206E-11
   30  AL                1.113E-07  1.059E-18 5.049E-19    -18.29680      .476785        .3217           0
    2  H2O                       0 -4.271E-06 9.998E-01      -.00010     1.000000        .0001   4.930E-32
  990  SOH1                      0 -7.820E-06 1.000E+00            0     1.000000            0           0
  140  CO3               3.985E-03  2.499E-05 1.745E-05     -4.75815      .698440        .1559           0
  460  MG                1.111E-03  2.417E-04 1.710E-04     -3.76693      .707732        .1501           0
  330  H                         0 -1.892E-03 4.074E-09     -8.39000      .920997       8.3900   6.019E-36
```

(continued)

## TABLE 5.8 (continued)

```
SPECIES:   TYPE  I - COMPONENTS

  ID         NAME          CALC MOL   ACTIVITY   LOG ACTVTY     GAMMA    NEW LOGK       DH
  150  CA                  2.726E-04  1.920E-04    -3.71676   .704245       .152        0
  460  MG                  2.417E-04  1.710E-04    -3.76693   .707752       .150        0
  500  NA                  2.982E-03  2.721E-03    -2.56532   .912428       .040        0
  140  CO3                 2.499E-05  1.745E-05    -4.75815   .698440       .156        0
  732  SO4                 1.779E-03  1.225E-03    -2.91171   .688888       .162        0
  180  CL                  9.879E-04  8.982E-04    -3.04662   .909190       .041        0
   30  AL                  1.059E-18  5.049E-19   -18.29680   .476785       .322        0
   90  H3BO3               8.122E-06  8.136E-06    -5.08957  1.001794      -.001        0
  410  K                   4.314E-04  3.922E-04    -3.40649   .909190       .041        0
  580  PO4                 2.781E-11  1.230E-11   -10.91013   .442322       .354        0
  770  H4SIO4              4.440E-07  4.447E-07    -6.35189  1.001794      -.001        0
  490  NH4                 9.711E-07  8.815E-07    -6.05476   .907773       .042        0
  270  F                   1.975E-04  1.798E-04    -3.74530   .910088       .041        0
  231  CU+2                6.606E-10  4.639E-10    -9.33359   .702165       .154        0
  950  ZN                  3.442E-08  2.417E-08    -7.61681   .702165       .154        0


SPECIES:   TYPE  II - COMPLEXES

  ID         NAME          CALC MOL   ACTIVITY   LOG ACTVTY     GAMMA    NEW LOGK       DH
9909501  SOH-ZN            7.820E-06  7.820E-06    -5.10681  1.000000      2.510        0
3305800  HPO4 -2           1.597E-07  1.111E-07    -6.95413   .695906     12.503   -3.530
3305801  H2PO4 -           7.977E-09  7.292E-09    -8.13713   .914181     19.592   -4.520
3300020  OH-               2.709E-06  2.465E-06    -5.60810   .910088    -13.957   13.345
3307700  H3SIO4 -          1.412E-08  1.286E-08    -7.89067   .911203     -9.888    8.935
3307701  H2SIO4 -2         9.276E-12  6.479E-12   -11.18850   .698440    -21.461   29.714
7702700  SIF6 -2           8.998E-33  6.262E-33   -32.20328   .695906     30.337  -16.260
3300900  H2BO3 -1          1.264E-06  1.147E-06    -5.94037   .907773     -9.199    3.224
 902700  BF(OH)3 -         6.429E-10  5.836E-10    -9.23387   .907773      -.357    1.850
 902701  BF2(OH)2 -        5.035E-14  4.570E-14   -13.34007   .907773      7.672    1.635
 902702  BF3OH -           4.016E-20  3.645E-20   -19.43827   .907773     13.709   -1.580
 902703  BF4 -             1.180E-25  1.080E-25   -24.96647   .907773     20.316   -1.795
3304900  NH3 AQ            1.232E-07  1.234E-07    -6.90867  1.001794     -9.245   12.480
4907320  NH4SO4 -          1.524E-08  1.392E-08    -7.85647   .913351      1.149        0
4603300  MGOH +            7.530E-08  6.900E-08    -7.16114   .916385    -11.746   15.935
4602700  MGF +             2.227E-06  2.031E-06    -5.69222   .912290      1.860    4.674
4601400  MGCO3 AQ          2.844E-06  2.849E-06    -5.54534  1.001794      2.979    2.022
4601401  MGHCO3 +          3.315E-06  3.020E-06    -5.51995   .911203     11.436   -2.430
4607320  MGSO4 AQ          3.720E-05  3.727E-05    -4.42863  1.001794      2.249    1.399
4605800  MGPO4 -           8.931E-09  8.165E-09    -8.08805   .914181      6.628    3.100
4605801  MGH2PO4 +         4.445E-11  4.064E-11   -10.39105   .914181     21.105   -1.120
4605802  MGHPO4 AQ         1.420E-08  1.422E-08    -7.84705  1.001794     15.219    -.230
1503300  CAOH +            1.299E-08  1.189E-08    -7.92488   .915398    -12.560   14.535
1501400  CAHCO3 +          3.300E-06  3.021E-06    -5.51984   .915398     11.383    1.790
1501401  CACO3 AQ          4.752E-06  4.761E-06    -5.32232  1.001794      3.152    4.030
1507320  CASO4 AQ          4.783E-05  4.792E-05    -4.31949  1.001794      2.308    1.470
1505800  CAHPO4 AQ         1.168E-08  1.170E-08    -7.93191  1.001794     15.084    -.230
1505801  CAPO4 -           7.431E-09  6.793E-09    -8.16791   .914181      6.498    3.100
1505802  CAH2PO4 +         3.909E-11  3.573E-11   -10.44691   .914181     20.999   -1.120
1502700  CAF +             3.291E-07  3.006E-07    -6.52208   .913351       .979    3.798
5001400  NACO3 -           9.627E-07  8.801E-07    -6.05547   .914181      1.307    8.911
5001401  NAHCO3 AQ         2.321E-06  2.326E-06    -5.63347  1.001794     10.079        0
5007320  NASO4 -           1.828E-05  1.671E-05    -4.77703   .914181       .739    1.120
5005800  NAHPO4 -          6.449E-10  5.896E-10    -9.22945   .914181     12.675        0
5002700  NAF AQ            7.918E-08  7.932E-08    -7.10062  1.001794      -.791        0
4107320  KSO4 -            3.695E-06  3.378E-06    -5.47139   .914181       .886    2.250
4105800  KHPO4 -           9.383E-11  8.578E-11   -10.06662   .914181     12.679        0
 303300  ALOH +2           1.815E-15  1.268E-15   -14.89690   .698440     -4.834   11.899
 303301  AL(OH)2 +         2.642E-12  2.415E-12   -11.61700   .914181    -10.061        0
 303302  AL(OH)4 -         2.008E-08  1.831E-08    -7.73720   .912290    -22.960   44.060
 302700  ALF +2            1.330E-15  9.288E-16   -15.03210   .698440      7.166        0
 302701  ALF2 +            1.004E-13  9.175E-14   -13.03740   .914181     12.789   20.000
 302702  ALF3 AQ           3.066E-13  3.071E-13   -12.51270  1.001794     17.019    2.500
 302703  ALF4 -            3.033E-14  2.767E-14   -13.55800   .912290     19.760        0
 307320  ALSO4 +           7.102E-19  6.479E-19   -18.18851   .912290      3.060    2.150
 307321  AL(SO4)2 -        6.913E-20  6.306E-20   -19.20022   .912290      4.960    2.840
 303303  AL(OH)3 AQ        7.449E-10  7.463E-10    -9.12710  1.001794    -16.001        0
2311400  CUCO3 AQ          4.340E-08  4.348E-08    -7.36174  1.001794      6.729        0
2311401  CU(CO3)2-2        1.384E-09  9.552E-10    -9.01988   .690417      9.991        0
2311800  CUCL +            1.231E-12  1.121E-12   -11.95021   .911203       .470    8.650
2311801  CUCL2 AQ          5.400E-16  5.410E-16   -15.26683  1.001794       .159   10.560
2311802  CUCL3 -           1.892E-21  1.724E-21   -20.76345   .911203     -2.250   13.690
2311803  CUCL4 -2          1.115E-26  7.761E-27   -26.11007   .695906     -4.433   17.780
2312700  CUF +             1.665E-12  1.517E-12   -11.81889   .911544      1.300    1.620
2313300  CUOH +            1.249E-09  1.138E-09    -8.94369   .911203     -7.960        0
2313301  CU(OH)2 AQ        5.827E-07  5.837E-07    -6.23379  1.001794    -13.681        0
2313302  CU(OH)3 -         9.492E-12  8.652E-12   -11.06289   .911544    -26.859        0
2313303  CU(OH)4 -2        6.122E-16  4.227E-16   -15.37399   .690417    -39.439        0
2313304  CU2(OH)2+2        8.222E-13  5.677E-13   -12.24589   .690417    -10.198   17.539
2317320  CUSO4 AQ          1.159E-10  1.161E-10    -9.93530  1.001794      2.309    1.220
2311402  CUHCO3 +          3.618E-10  3.298E-10    -9.48174   .911544     13.040        0
9501800  ZNCL +            6.411E-11  5.842E-11   -10.23343   .911203       .470    7.790
9501801  ZNCL2 AQ          5.485E-14  5.495E-14   -13.26005  1.001794       .449    8.500
9501802  ZNCL3 -           6.077E-17  5.538E-17   -16.25667   .911203       .540    9.560
9501803  ZNCL4 -2          3.574E-20  2.487E-20   -19.60429   .695906       .356   10.960
9502700  ZNF +             6.731E-11  6.136E-11   -10.21211   .911544      1.190    2.220
9503300  ZNOH +            7.134E-09  6.503E-09    -8.18691   .911544     -8.920   13.399
```

(continued)

Reproduced from
best available copy.

## TABLE 5.8 (continued)

```
9503301  ZN(OH)2 AQ      1.833E-08  1.836E-08   -7.73601   1.001794    -16.900          0
9503302  ZN(OH)3 -       1.564E-11  1.425E-11  -10.84611    .911544    -28.359          0
9503303  ZN(OH)4 -2      8.029E-16  5.544E-16  -15.25621    .690417    -41.038          0
9501804  ZNOHCL AQ       1.761E-10  1.764E-10   -9.75353   1.001794     -7.481          0
9507320  ZNSO4 AQ        6.930E-09  6.942E-09   -8.15852   1.001794      2.369      1.360
9507321  ZN(SO4)2-2      1.002E-10  6.915E-11  -10.16023    .690417      3.441          0
9501400  ZNHCO3 +        4.734E-09  4.316E-09   -8.36496    .911544     12.440          0
9501401  ZNCO3 AQ        8.400E-08  8.415E-08   -7.07496   1.001794      5.299          0
9501402  ZN(CO3)2-2      4.548E-08  3.140E-08   -7.50311    .690417      9.791          0
3301400  HCO3 -          1.661E-03  1.519E-03   -2.81858    .914181     10.369     -3.617
3301401  H2CO3 AQ        1.360E-05  1.363E-05   -4.86553   1.001794     16.678     -2.247
3307320  HSO4 -          5.312E-10  4.846E-10   -9.31464    .912290      2.027      4.910
3302700  HF AQ           1.079E-09  1.081E-09   -8.96630   1.001794      3.168      3.460
3302701  HF2 -           8.116E-13  7.386E-13  -12.13160    .910088      3.790      4.550
3302702  H2F2 AQ         3.138E-18  3.143E-18  -17.50260   1.001794      6.767          0


    SPECIES:   TYPE  III - FIXED SOLIDS

   ID         NAME          CALC MOL      LOG MOL    NEW LOGK        DH
      2  H2O              -4.271E-06       -5.369        .000            0
    330  H                -1.692E-03       -2.772       8.390            0
    890  SOH1             -7.820E-06       -5.107           0            0


    SPECIES:   TYPE  IV - PRECIPITATED SOLIDS

   ID         NAME          CALC MOL      LOG MOL    NEW LOGK        DH
5015001  CALCITE           6.198E-04       -3.208       8.475        2.585
5015002  DOLOMITE          8.239E-04       -3.084      17.000        8.290
2003002  DIASPORE          9.044E-08       -7.044      -6.873       24.630


    SPECIES:   TYPE  V - DISSOLVED SOLIDS

   ID         NAME          CALC MOL      LOG MOL    NEW LOGK        DH
2023101  TENORITE          6.704E-01        -.174      -7.620       15.240


    SPECIES:   TYPE  VI - SPECIES NOT CONSIDERED

   ID         NAME          CALC MOL      LOG MOL    NEW LOGK        DH
3301403  CO2(GAS)          4.187E-04       -3.378      18.160        -.530

  PERCENTAGE DISTRIBUTION OF COMPONENTS


CA
         82.9     PERCENT BOUND IN SPECIES     150   CA
          1.0     PERCENT BOUND IN SPECIES 1501400   CAHCO3 +
          1.4     PERCENT BOUND IN SPECIES 1501401   CACO3 AQ
         14.5     PERCENT BOUND IN SPECIES 1507320   CASO4 AQ


CU+2
          6.9     PERCENT BOUND IN SPECIES 2311400   CUCO3 AQ
         92.5     PERCENT BOUND IN SPECIES 2313301   CU(OH)2 AQ


NA
         99.3     PERCENT BOUND IN SPECIES     500   NA


ZN
         97.5     PERCENT BOUND IN SPECIES 9909501   SOH-ZN
          1.0     PERCENT BOUND IN SPECIES 9501401   ZNCO3 AQ


SO4
         94.3     PERCENT BOUND IN SPECIES     732   SO4
          2.0     PERCENT BOUND IN SPECIES 4607320   MGSO4 AQ
          2.5     PERCENT BOUND IN SPECIES 1507320   CASO4 AQ


CL
        100.0     PERCENT BOUND IN SPECIES     180   CL


F
         98.7     PERCENT BOUND IN SPECIES     270   F
          1.1     PERCENT BOUND IN SPECIES 4602700   MGF +


H3BO3
         86.5     PERCENT BOUND IN SPECIES      90   H3BO3
         13.5     PERCENT BOUND IN SPECIES 3300900   H2BO3 -1
```

(continued)

## TABLE 5.8 (continued)

```
K
          99.2      PERCENT BOUND IN SPECIES     410   K


PO4
          75.8      PERCENT BOUND IN SPECIES 3305800   HPO4 -2
           3.8      PERCENT BOUND IN SPECIES 3305801   H2PO4 -
           4.2      PERCENT BOUND IN SPECIES 4605800   MGPO4 -
           6.7      PERCENT BOUND IN SPECIES 4605802   MGHPO4 AQ
           5.5      PERCENT BOUND IN SPECIES 1505800   CAHPO4 AQ
           3.5      PERCENT BOUND IN SPECIES 1505801   CAPO4 -


H4SIO4
          96.9      PERCENT BOUND IN SPECIES     770   H4SIO4
           3.1      PERCENT BOUND IN SPECIES 3307700   H3SIO4 -


NH4
          87.5      PERCENT BOUND IN SPECIES     490   NH4
          11.1      PERCENT BOUND IN SPECIES 3304900   NH3 AQ
           1.4      PERCENT BOUND IN SPECIES 4907320   NH4SO4 -


AL
          96.4      PERCENT BOUND IN SPECIES  303302   AL(OH)4 -
           3.6      PERCENT BOUND IN SPECIES  303303   AL(OH)3 AQ


H2O
          66.2      PERCENT BOUND IN SPECIES 3300020   OH-
           1.8      PERCENT BOUND IN SPECIES 4603300   MGOH +
           2.0      PERCENT BOUND IN SPECIES  303302   AL(OH)4 -
          28.5      PERCENT BOUND IN SPECIES 2313301   CU(OH)2 AQ


SOH1
         100.0      PERCENT BOUND IN SPECIES 9909501   SOH-ZN


CO3
           1.5      PERCENT BOUND IN SPECIES     140   CO3
          96.7      PERCENT BOUND IN SPECIES 3301400   HCO3 -


MG
          84.1      PERCENT BOUND IN SPECIES     460   MG
           1.2      PERCENT BOUND IN SPECIES 4601401   MGHCO3 +
          12.9      PERCENT BOUND IN SPECIES 4607320   MGSO4 AQ


H
          98.2      PERCENT BOUND IN SPECIES 3301400   HCO3 -
           1.6      PERCENT BOUND IN SPECIES 3301401   H2CO3 AQ
  IDX        NAME          AQUEOUS MASS  SORBED MASS     PRECIPITATED MASS
   150  CA                  3.288E-04          0             1.444E-03
   231  CU+2                6.299E-07          0                 0
   500  NA                  3.003E-03          0                 0
   950  ZN                  2.014E-07      7.820E-06             0
   732  SO4                 1.886E-03          0                 0
   180  CL                  9.879E-04          0                 0
   270  F                   2.002E-04          0                 0
    90  H3BO3               9.386E-06          0                 0
   410  K                   4.351E-04          0                 0
   580  PO4                 2.108E-07          0                 0
   770  H4SIO4              4.581E-07          0                 0
   490  NH4                 1.110E-06          0                 0
    30  AL                  2.082E-08          0             9.044E-08
     2  H2O                 4.091E-06          0             1.809E-07
   140  CO3                 1.718E-03          0             2.268E-03
   460  MG                  2.873E-04          0             8.239E-04
   330  H                   1.692E-03          0            -2.713E-07
```

minimum log K, maximum log K, log ion activity product (log IAP) and enthalpy of reaction.

MINTEQ activity Kd runs for Zn were obtained for the specific pH conditions and their corresponding total metal treatments. In order to evaluate how well MINTEQ predicted the laboratory adsorption results, the output corresponding to Section VI was used. The molar values of the sorbed mass (particulate) and aqueous (dissolved) masses were compared the actual experimental results from the pH = 8.39 data set that conformed to the linear Kd approach. Figures 5.9 & 5.10 show the comparison plot of the MINTEQ prediction versus actual laboratory results for both dissolved and particulate Zn.

If the system being modeled has a relatively constant pH and the metal variation is not too great (> 2x), the activity Kd approach would give satisfactory results. However, if pH, metal level, SS and other parameters change dramatically, then one of the other adsorption routines should be selected. For example, zinc adsorption in White River samples at pH = 7.50 and 6.70 showed a non-linear behavior when plotted to yield the "activity" Kd (Figures 5.11 & 5.12). The curvilinear relationship observed is more characteristic of a Langmuir behavior. In most situations, however, the metal level is low enough that the linear portion could be used to calculate a Kd. Lead adsorption was linear in all pH ranges tested (6.40, 6.80, 7.30, 8.12, and 8.90) and nickel adsorption appeared to also show a linear relation between $1/\{Ni^{+2}\}$ and particulate Ni. A summary of the log Kd's as a function of pH for the White River are shown in Figure 5.13.

## 5.7 ACTIVITY LANGMUIR MODELING WITH MINTEQ

The Langmuir model can often be used to predict metal sorption in natural systems. The previous data for zinc (Figures 5.11 & 5.12) indicated that a Langmuir equation might be appropriate. The equation can be used to fit data that resembles the curve shown in Figure 5.14. At low $\{Cu^{+2}\}$, the equation is linear, while at very high $\{Cu^{+2}\}$, the equation represents a saturation of surface sites (CuS = ST). The equation could be used over a wide range of $\{Cu^{+2}\}$'s and could account for different site availability by variation of ST (maximum surface coverage). This equation would be very useful on the White River where large fluctuations in suspended solids and ambient dissolved copper are observed. Metal partitioning to solids is more significant in the water column, as opposed to bed sediments and thus, dissolved metal should be related to suspended sediment (and responsive to ST in the Langmuir equation). As metal partitioning becomes more dominated by bed sediment interaction, the usefulness of the

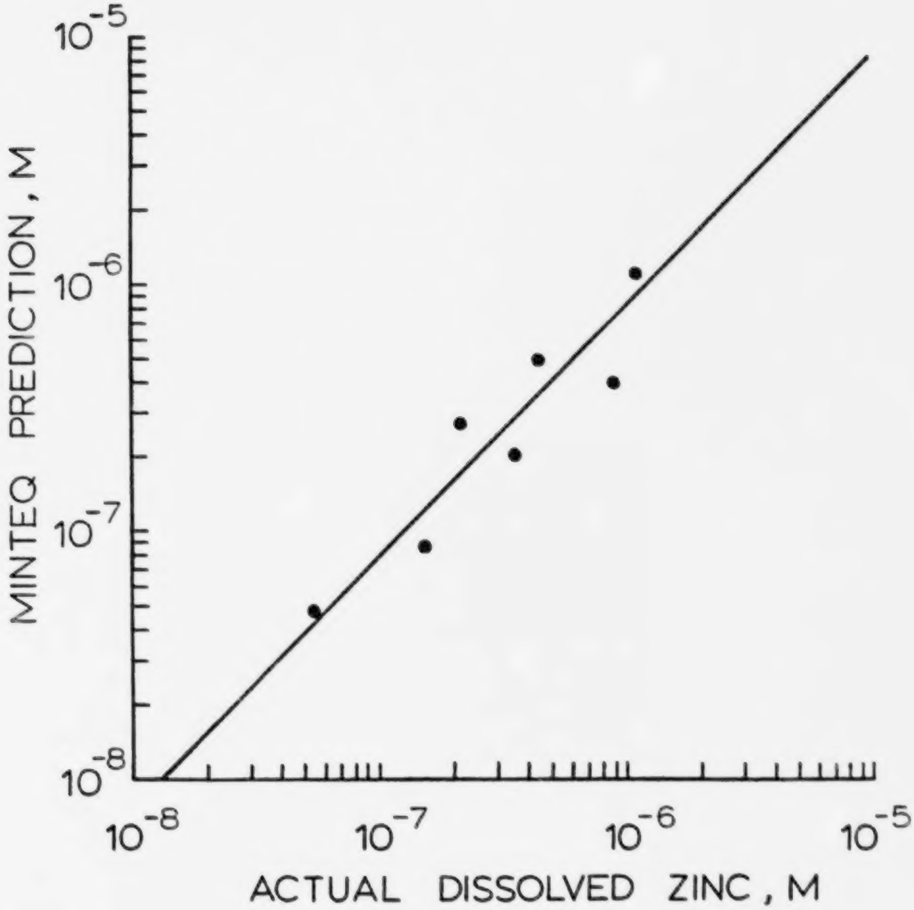


Figure 5.9 Actual dissolved Zinc vs. MINTEQ prediction.

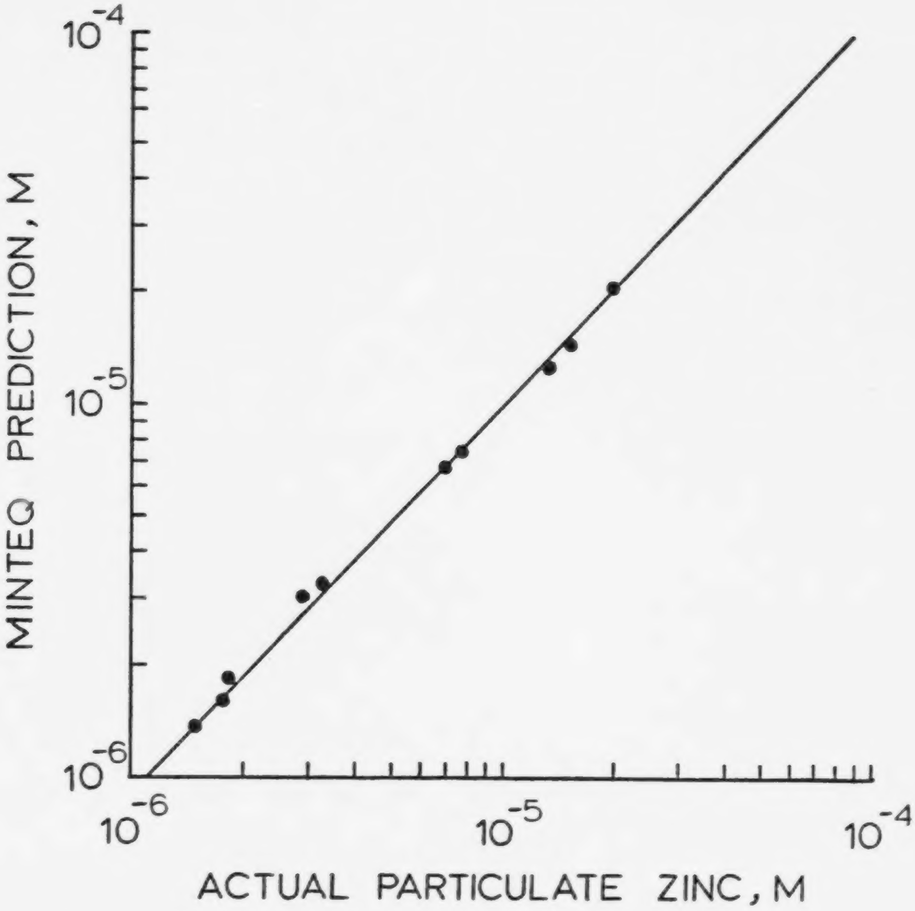


Figure 5.10 Actual particulate Zn vs. MINTEQ prediction.

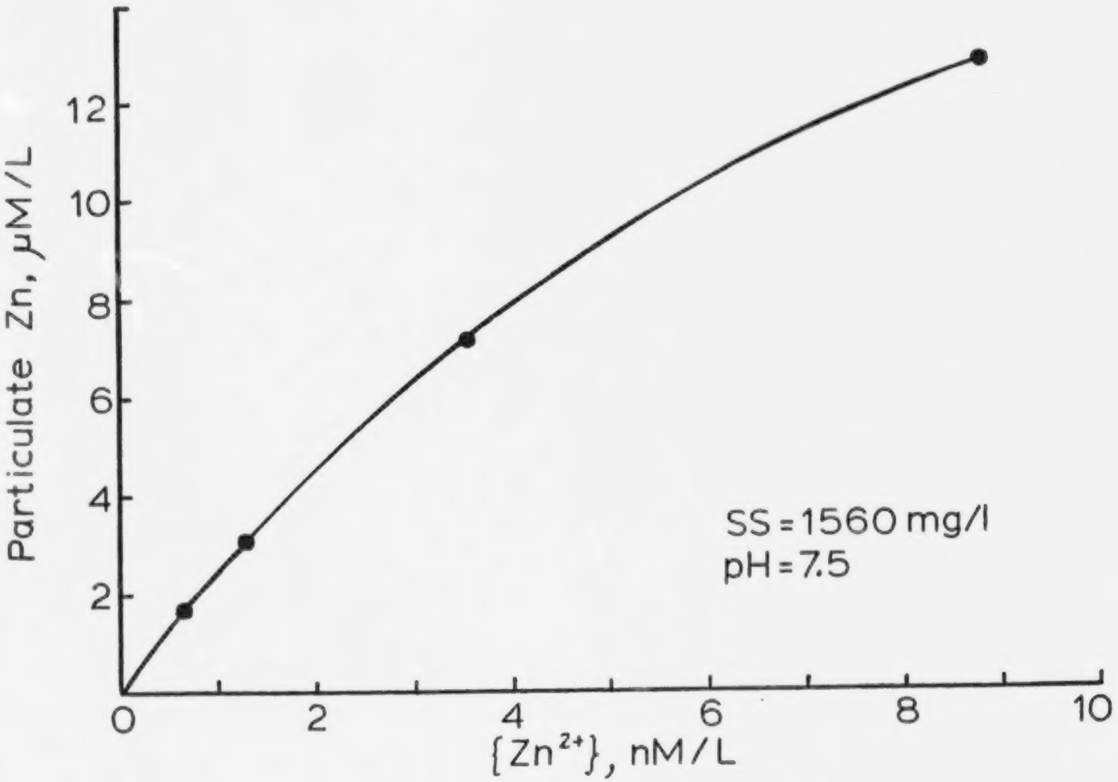


Figure 5.11 Zn ion activity vs. particulate Zn, pH = 7.5.

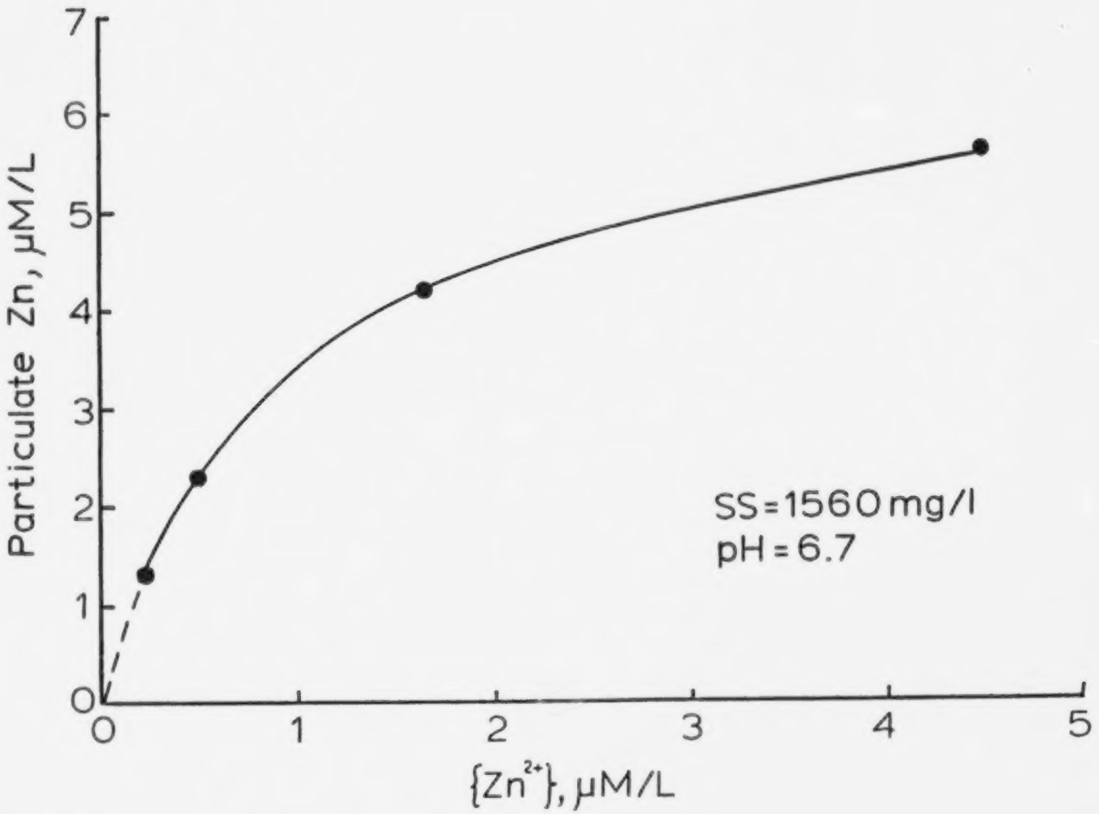


Figure 5.12 Zn ion activity vs. particulate Zn, pH = 6.7.

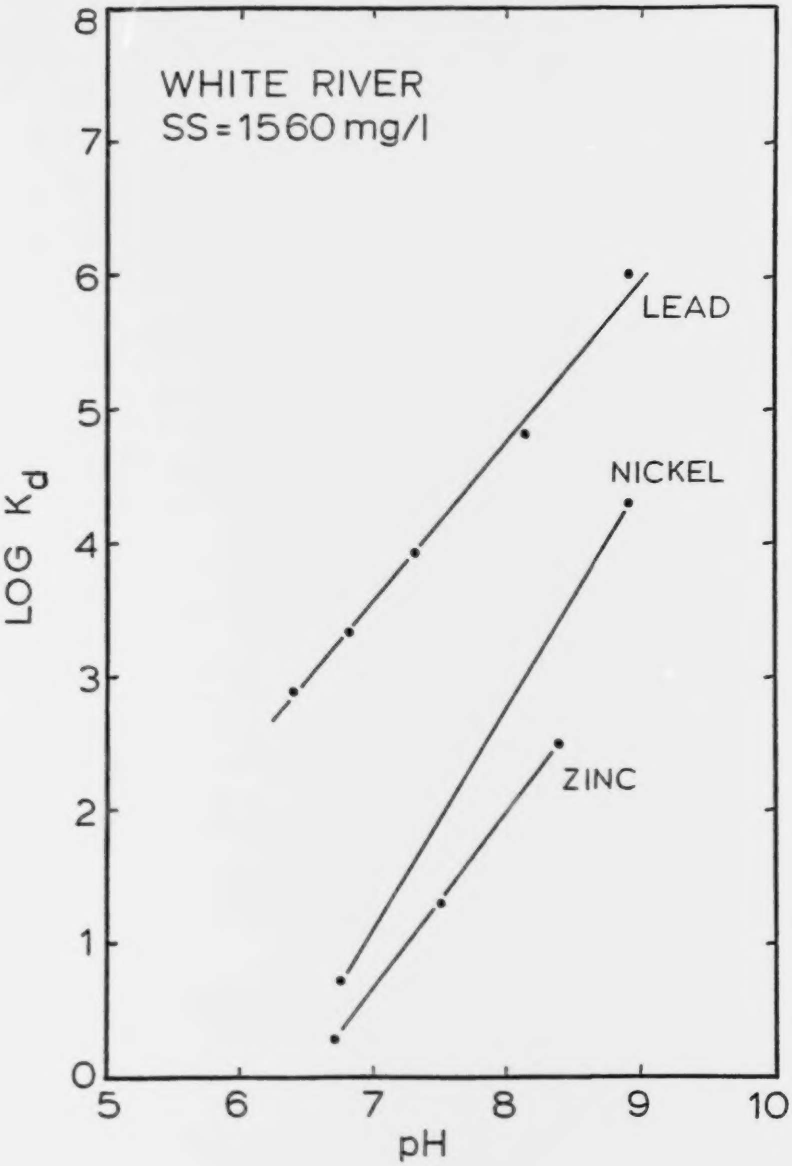
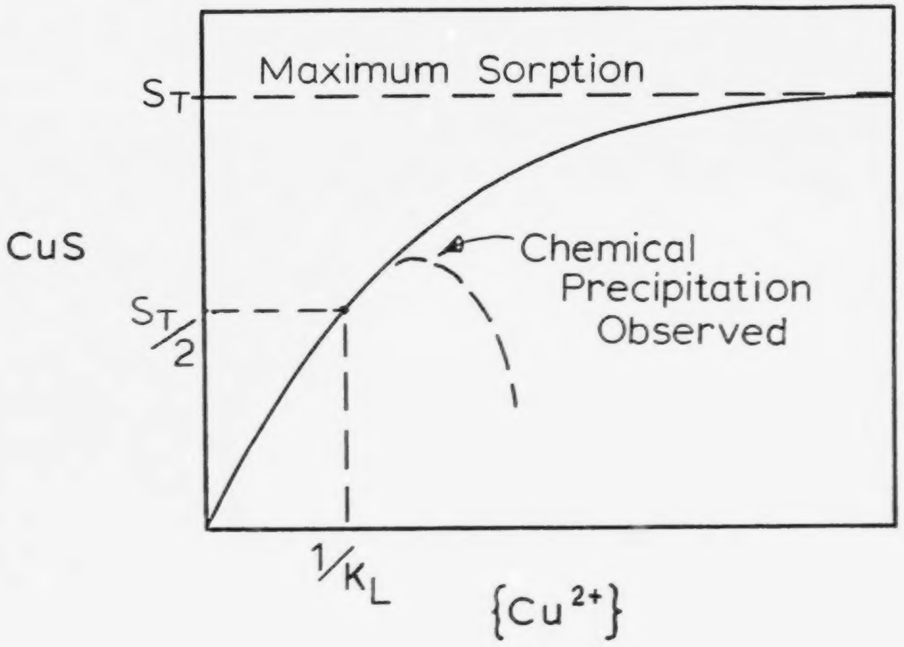


Figure 5.13 Log Kd's vs. pH for Zn, Ni and Pb.

# ACTIVITY LANGMUIR PLOT

$$CuS = \frac{K_L S_T \{Cu^{2+}\}}{1 + K_L \{Cu^{2+}\}}$$



$$\frac{1}{CuS} = \frac{1}{K_L S_T} \cdot \frac{1}{\{Cu^{2+}\}} + \frac{1}{S_T} \quad \text{Linear Form}$$

Figure 5.14 General Langmuir adsorption plot.

Langmuir decreases and the activity Kd might be entirely appropriate.

To obtain data to use the Langmuir model, sufficient amounts of metal need to be added to saturate (or nearly saturate) the surface sites. This is often difficult when working with highly turbid surface waters (100 mg SS/l and greater) in-situ or in sediment-water reactors. It was observed, on more than one occasion, that chemical precipitation (malachite, zinc carbonate, willemite) occurred before the system could approach maximum site coverage. The effect on experimental results is illustrated with the dashed line in Figure 5.14. Removal of suspended solids (centrification) or dilution (i.e. reduce available sites) may allow a saturation at a lower $\{Cu^{+2}\}$, but this did not work on the White River, even with a reduction of suspended solids by an order of magnitude (1600 mg/l to 100 mg/l).

An experiment using the White River with pH = 7.5 and SS = 200 mg/l illustrated the lower section of a Langmuir type fit (Figure 5.15). Attempts to increase the range of the plot by Cu addition only resulted in malachite precipitation. A plot of the linearized equation (Figure 5.16) showed a curvilinear relation when a straight line would be anticipated if data fit a Langmuir model. At this point, it is emphasized that the MINTEQ input files were only considering inorganic speciation of the metal. No organics were used even through the White River contains 5 - 7 mg/l of dissolved organic carbon (DOC, see Table 5.4). The curvilinear relation could result from omission of organic complexation, an effect which would be most pronounced at low $\{Cu^{+2}\}$ or high $1/\{Cu^{+2}\}$ (on Figure 5.16). Addition of EDTA simulates the effect of natural organic complexation on the {Cu+2} calculation by MINTEQ. The optimum fit (linear) was obtained with 55 ug/l of EDTA (10-M). Using this organic level for two other experiments at pH = 6.7 and 8.3 gave linear plots (Figure 5.16) indicating that this artificial specification of an organic compexing agent (EDTA) might be a reasonable substitute for actual complexing organics in the test water. The curvilinear nature observed in these experiments (without EDTA) is not due to lack of consideration of desorbed ions in the equilibrium solution. Under the conditions of the experiment (addition of <1mg/l of metal), background concentrations of $Ca^{+2}$, $Mg^{+2}$, $Na^{+}$, etc. would appear essentially unchanged in the White River matrix (Table 5.4) by release due to an ion exchange phenomenon. The slope of the lines for pH = 6.7, 7.5 and 8.3 and estimates for ST from the experiments allowed a determination of the Langmuir Constant, KL. The results (Table 5.9, Figure 5.17 indicate that the metal adsorption phenomena in the White River can be adequately described using kinetics based on the mass of solids, the dissolved (free) metal, the available sites and pH, and, that equilibrium metal experiments can be

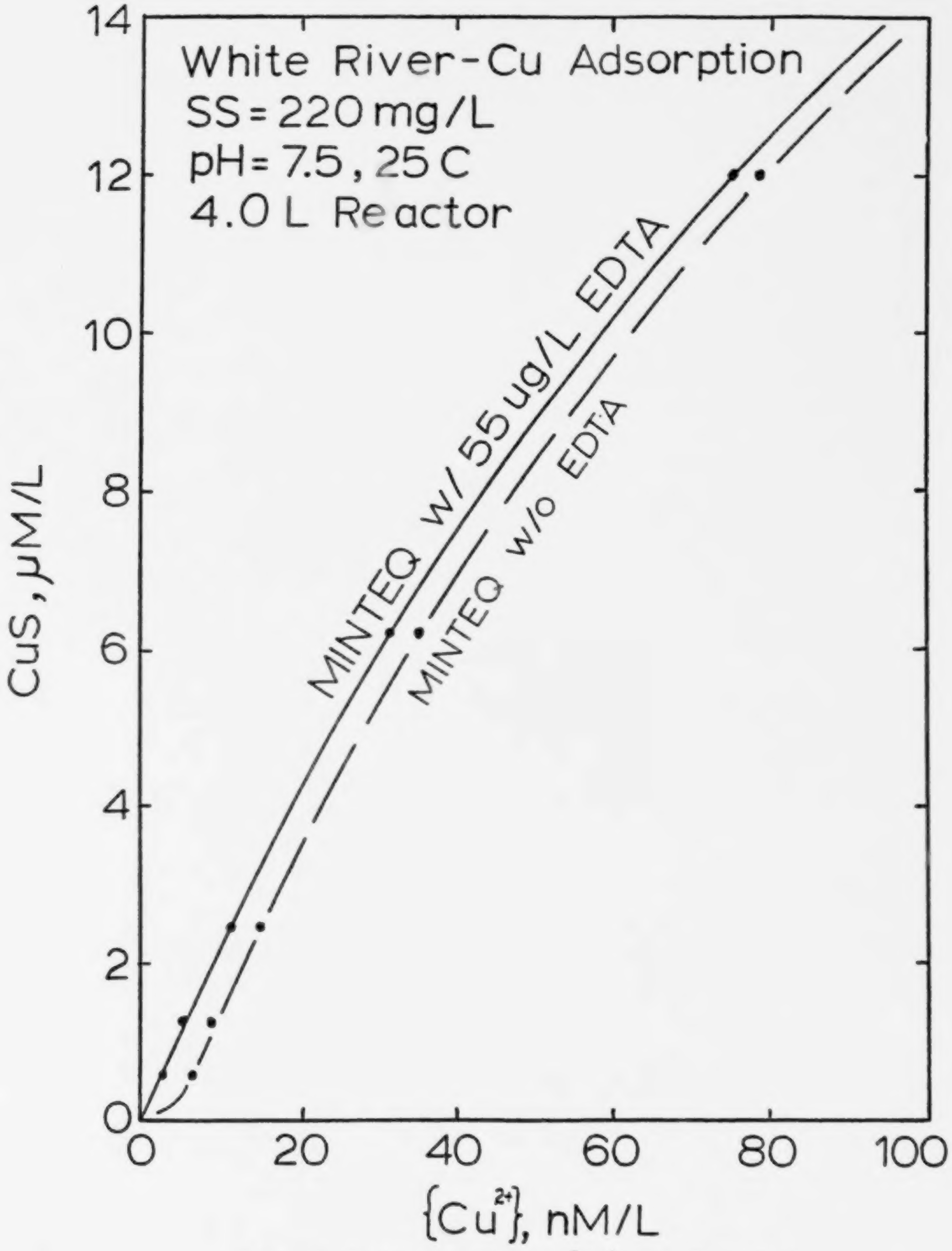


Figure 5.15 CuS vs. {Cu}, pH = 7.5.

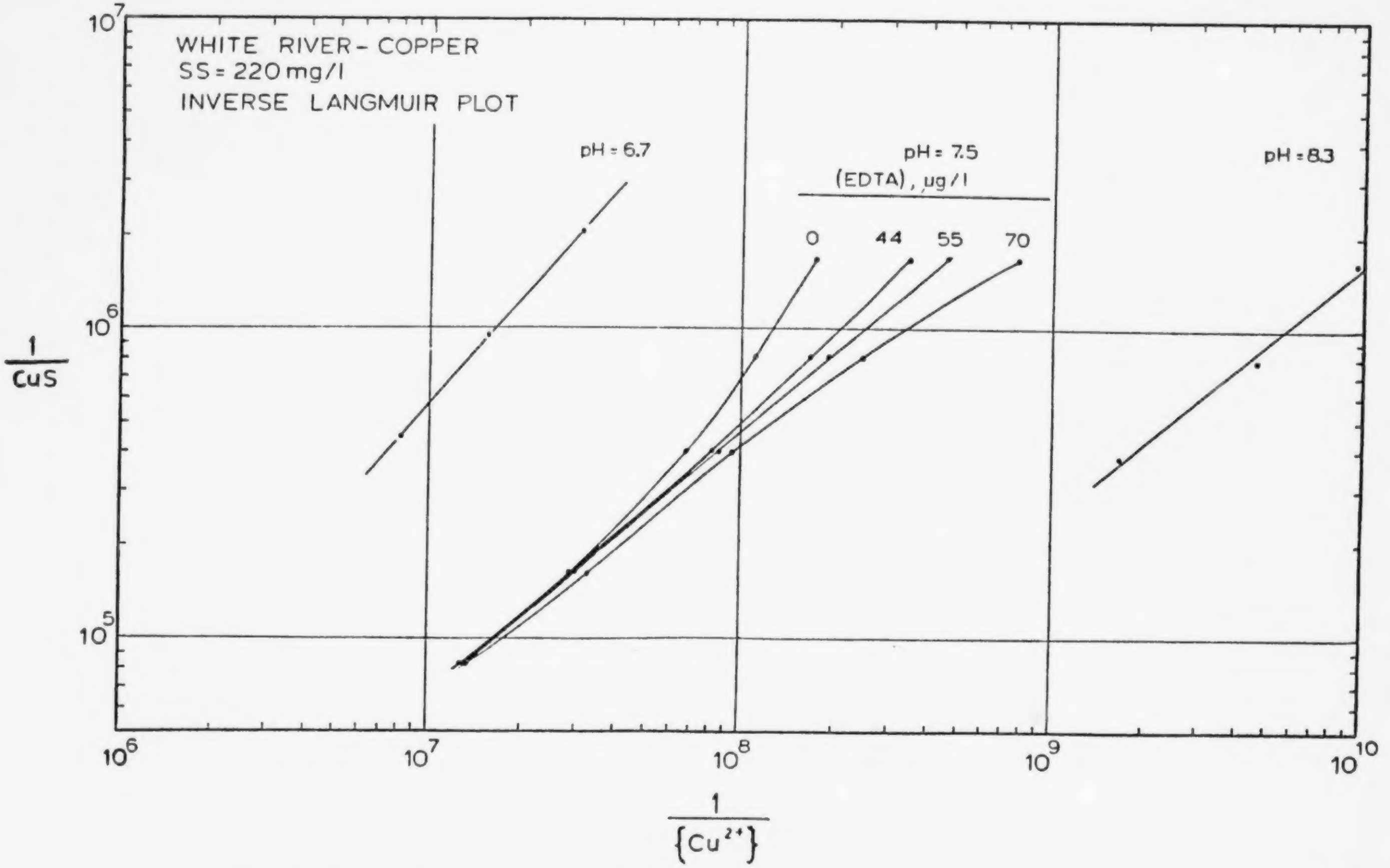


Figure 5.16 Linear Langmuir plot of data obtained for the White River at a suspended solids concentration of 220 mg/1, pH between 6.7 and 8.3. The {Cu} was first calculated by MINTEQ at pH=7.5 and then various increments of EDTA were added until a linear plot resulted. The constants are shown in Table 26.

TABLE 5.9 SUMMARY OF ADSORPTION MODELING IN THE WHITE RIVER-LANGMUIR CONSTANTS AND ACTIVITY Kd FOR COPPER PARTITIONING

| SS, mg/l | pH | Activity Langmuir Model | | | Activity |
|---|---|---|---|---|---|
| | | $K_L S_T$ | $S_T$, M/L | $K_L$, L/M | $K_d$ |
| 220 | 6.70 | 14.3 | - | - | - |
| 220 | 7.50 | 243. | 3.3 E-05 | 7.36 E+06 | - |
| 220 | 8.30 | 6 090. | - | - | - |
| 1590 | 6.80 | 186. | - | - | 8.29 |
| 1590 | 7.46 | 800. | - | - | 575. |
| 1590 | 8.31 | 19 300 | - | - | 17 000 |
| 1590 | 8.95 | 136 000 | - | - | 933 000 |

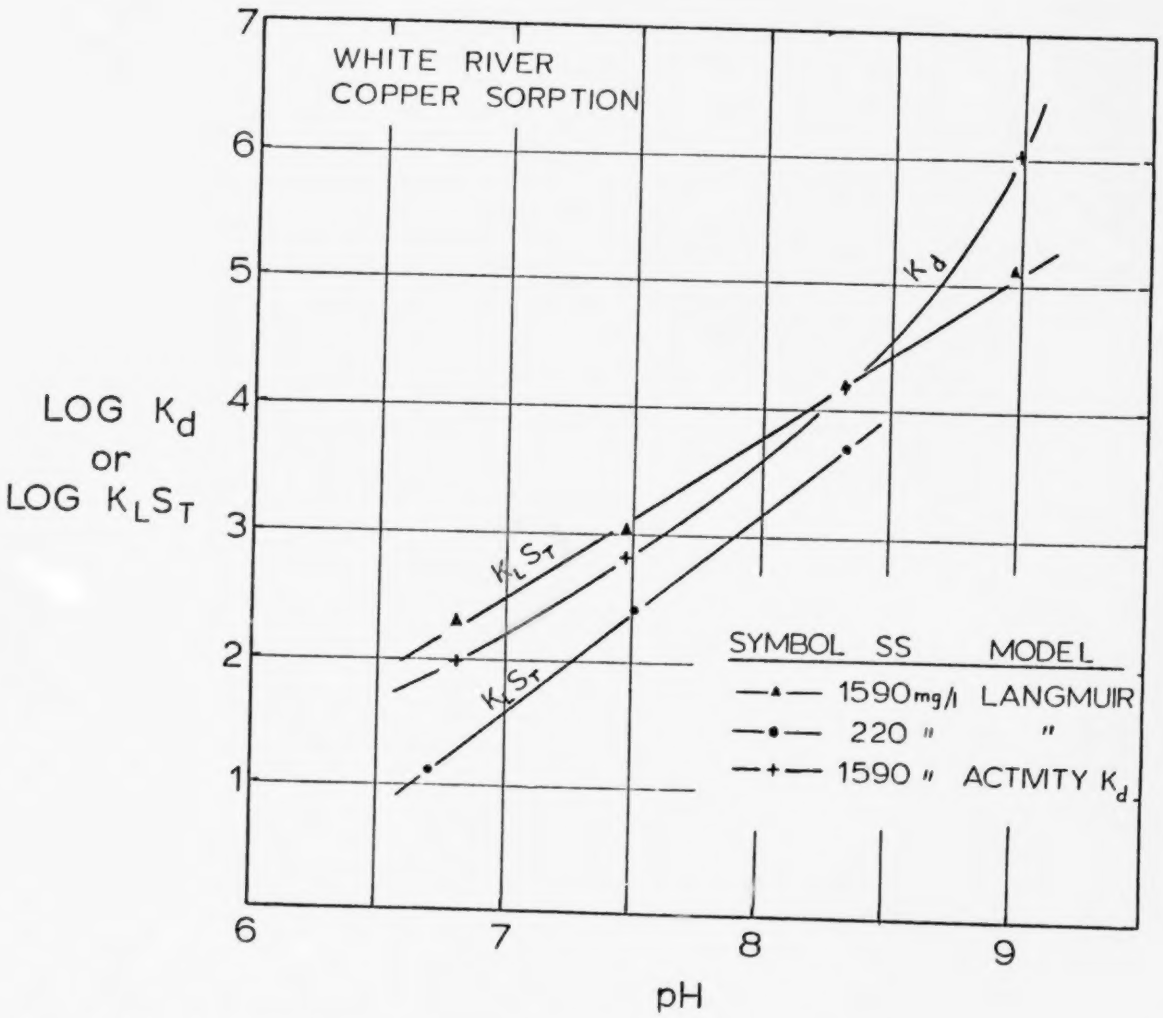


Figure 5.17 Langmuir constants ($K_LS_T$) and the activity Kd values as a function of pH in the White River.

fit to an "activity" Langmuir Isotherm. The experiments at pH = 6.7 and 8.3 did not have sufficient data to permit precise estimates of ST and KL and the values in the table should be regarded as estimates. It is essential that continued development of methods for determining dissolved metal species be encouraged and that organic speciation of metals be considered in modeling systems highly transitory in flow and water quality, such as that observed in the White River.

## 5.8 CONCLUSIONS

The White River study illustrated details regarding the development of a suitable chemical matrix, the selection, calibration and application of appropriate adsorption routines in MINTEQ. Both the activity Kd's and activity Langmuir routines were used to model laboratory and field data for Zn, Pb, Cu, and Ni. The most important aspects of adsorption modeling for these metals in the White River were the effects of pH, suspended solids concentration, ambient metal level and the flow regime on ultimate metal removal and aqueous concentration. As with most aquatic environments, the effect of organic complexation upon metal partitioning and chemical precipitation in the White River needs to be further examined.

# SECTION 6

# TEN MILE RIVER CASE STUDY

This case study of MEXAMS involves application to a wasteload allocation program on the Ten Mile River in Massachusetts. This river receives metal wastes at a number of points along its 22 mile length, and estimates of metal speciation within the river would be useful for determination of acceptable effluent limits to the basin. This application encountered data problems which limited the simulation to one run in which copper was modeled. This section documents the available data and associated problems, development of a preliminary input for MEXAMS application to a 15 mile stretch of the river, and corresponding model results. The case study is presented in detail appropriate to provide novice users insight into a number of aspects of metal speciation/transport modeling with MEXAMS.

## 6.1 BACKGROUND INFORMATION AND BASIN DESCRIPTION

The Ten Mile River is located in southeastern Massachusetts and eastern Rhode Island. A map of the basin is shown in Figure 6.1. The river has long experienced water quality problems due to the concentrations of manufacturing centers along the river. Disposal to the river includes numerous industrial - primarily metal finishing - wastes, treated municipal wastewater, and urban runoff. In 1968, the Massachusetts Division of Water Pollution Control (DWPC) identified 62 industrial waste discharges and two municipal sewage treatment plants, and subsequently undertook to abate pollution of Ten Mile River. A concentrated effort since that time has focused largely on conventional water quality problems in the basin. By 1973, all industrial discharges received some treatment, and albeit slower, progress has been made on municipal waste discharges.

In recent years, the question has been raised as to whether current inorganic industrial discharge limitations on Ten Mile River are adequate to attain or maintain acceptable water quality levels with regard to heavy metals. Also, the long

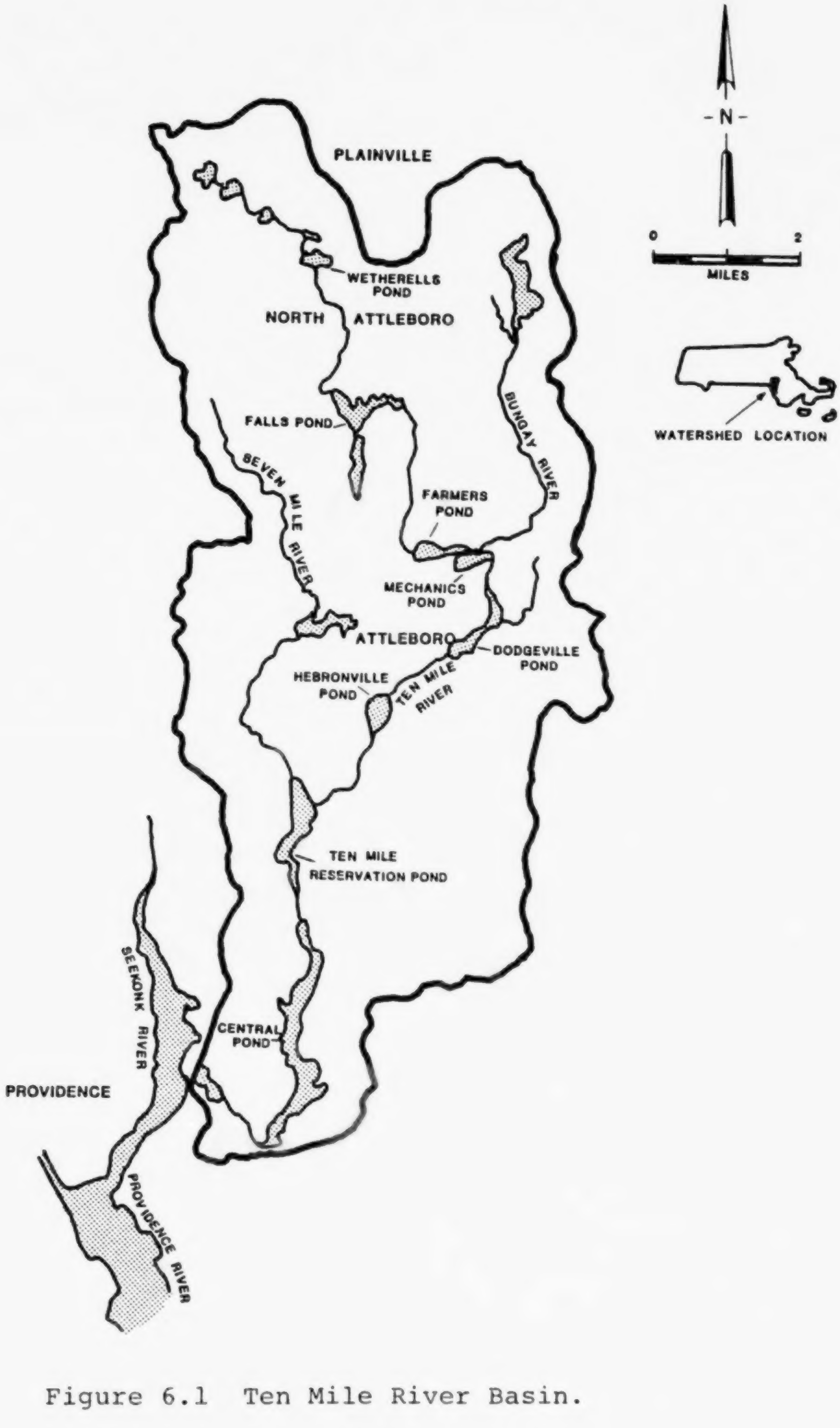

PLAINVILLE
WETHERELLS POND
NORTH ATTLEBORO
FALLS POND
SEVEN MILE RIVER
FARMERS POND
BUNGAY RIVER
MECHANICS POND
ATTLEBORO
DODGEVILLE POND
HEBRONVILLE POND
TEN MILE RIVER
TEN MILE RESERVATION POND
SEEKONK RIVER
CENTRAL POND
PROVIDENCE
PROVIDENCE RIVER
N
0
2
MILES
WATERSHED LOCATION

Figure 6.1 Ten Mile River Basin.

history of metal waste discharges has resulted in extremely high concentrations of heavy metals in the sediments of impoundments along the river. These sediments now act as additional sources of metals to the river during high flow periods.

Region 1 of EPA has established a wasteload allocation/total maximum daily load (WLA/TMDL) program to establish appropriate effluent limitations and guidelines for rivers in the region. To help predict whether a metal's discharge would interfere with attainment of acceptable water quality levels, it is useful to determine the fraction of metal that is potentially harmful (i.e., free metal) and the fraction of metal that is potentially complexed and relatively inert. Consequently, EPA has undertaken to apply MEXAMS to the Ten Mile River WLA program. An intensive water quality survey of Ten Mile River was scheduled for the summer of 1984 by the state of Massachusetts; this survey was intended to provide the necessary data for the MEXAMS application.

The Ten Mile River drains an area of 54 square miles in southeastern Massachusetts and eastern Rhode Island. Originating in Savage's Pond in Plainville, Massachusetts, the stream flows generally southwest through North Attleboro, Attleboro, and Seekonk to Pawtucket and East Providence, Rhode Island where it empties into the Seekonk River. The total length of the river is 22 miles. The elevation of the river bed drops from 230 feet above sea level to ten feet at the mouth for an average fall of ten feet per mile. Flow is highly restricted, with various dams creating a total of 15 impoundments. These impoundments comprise almost half the length of the river. Most of the remaining length is enclosed in concrete or masonry retaining walls.

There are two major tributaries to the Ten Mile River - the Bungay and Seven Mile Rivers. The former begins in North Attleboro and flows south approximately 5 miles to join the Ten Mile River above Mechanics Pond in Attleboro. The Seven Mile River flows south (for seven miles) from a marsh just east of North Attleboro center to join the Ten Mile River at the state line. In 1975, about 60,000 persons lived in the Massachusetts portion of the basin, primarily in the municipalities of Plainville, North Attleboro, Seekonk, and Attleboro. Urban development is most dense along the river. The basin has a temperate climate typical of coastal New England, with an average annual temperature of 50° F. Precipitation is generally well distributed throughout the year, averaging 44 inches of rainfall and 34 inches of snowfall annually.

## 6.2 TEN MILE RIVER DATA

The basic data required to execute MEXAMS for a system such as Ten Mile River are 1) detailed descriptions of the hydraulics, including flows and channel geometry, 2) dissolved and adsorbed concentrations of all major chemical species, and 3) loading rates of metals. This section presents the data utilized in the Ten Mile River Case Study along with data sources and major data limitations.

### 6.2.1 Data Sources

Most of the data available for this study were collected by the State of Massachusetts, Division of Water Pollution Control during flow and water quality surveys of the Ten Mile River in June - August, 1984 (Hogan, 1984, personal communication). In addition, some gaps in the survey were filled by consulting intensive surveys conducted in the past (Mass. DWPC, 1973, 1975, 1982). The 1984 surveys were partially designed to accomodate the MEXAMS input requirements, since EPA and the state DWPC were cooperatively interested in the model application.

In the 1984 surveys, water quality data were obtained at twenty-four river and tributary monitoring stations, nine impoundments, and twenty-one point source (industrial and municipal) discharges. Flow gaging stations were located at eight of the river basin water quality stations. Since there are no USGS gages on the river, crucial flow measurements are available only from the current and previous surveys conducted by the state. Tables 6.1 - 6.4 list all of the stations and their locations; Figure 6.2 shows the locations of the river monitoring stations, and Figure 6.3 shows the locations of point source discharges.

The 1984 data that are described in this document are preliminary (Hogan, 1984, personal communication); the data had not been completely analyzed and verified at the time this project was completed.

### 6.2.2 Hydraulics Data

River and tributary flow measurements at the stations listed in Table 6.3 were available for several dates in the summer of 1984. Due to periods of heavy rainfall prior to the surveys, all flows were significantly higher than base flows for the basin. In addition, the flows were steadily decreasing during

## TABLE 6.1 TEN MILE RIVER MONITORING STATIONS

| Station Number | Location | River Mile |
|---|---|---|
| TM01 | Fuller Street, Plainville | 20.7 |
| TM02 | West Bacon Street, Plainville | 19.8 |
| TM03 | Washington Street, Noth Attleborough | 18.8 |
| TM04 | Route 1, Inlet Falls Pond, North Attleborough | 17.4 |
| TM05 | Mount Hope Street, North Attleborough | 16.6 |
| TM06 | Cedar Street, North Attleborough | 15.6 |
| TM07 | West Street, Attleboro | 14.2 |
| TM07A | Mechanic Street, Attleboro | 13.4 |
| TM08 | County Street, Attleboro | 13.0 |
| TM08A | Olive Street, Attleboro | 12.6 |
| TM09 | Lamb Street, Attleboro | 12.3 |
| TM10 | Thatcher Street, Attleboro | 11.8 |
| TM11 | Tiffany Street, Attleboro | 10.7 |
| TM12 | Bridge Street, below dam, Attleboro | 9.4 |
| TM13 | Pond Street, Seekonk | 8.6 |
| TM14 | Central Avenue, Pawtucket, R.I. | 7.0 |
| TM15 | Armistice Boulevard, Pawtucket, R.I. | 5.8 |
| TM16 | Route 152, East Providence | 3.2 |
| TM17 | Roger Williams Avenue, East Providence, R.I. | 0.8 |
|  | Bungay River |  |
| BG02 | Holden Street, Attleboro | 14.0, 0.6 |
|  | Speedway Brook |  |
| SW00 | Maple Street, Attleboro | 11.9, 0.9 |
| SW01 | Route 152, Attleboro | 11.9, 0.1 |
|  | Seven Mile River |  |
| SM00 | Draper Avenue, North Attleborough | 7.5, 5.0 |
| SM01 | County Street, Attleboro | 7.5, 0.3 |

## TABLE 6.2 TEN MILE RIVER IMPOUNDMENT MONITORING LOCATIONS

| Impoundment | Location (Community) | River Mile |
|---|---|---|
| Fuller Pond | Plainville | 20.8-20.7 |
| Wetherells Pond | Plainville | 19.8-19.6 |
| Falls Pond (North) | North Attleborough | 17.4-16.7 |
| Farmers Pond | Attleboro | 14.5-14.3 |
| Mechanics Pond | Attleboro | 14.2-13.4 |
| Dodgeville Pond | Attleboro | 12.3-11.2 |
| Hebronville Pond | Attleboro | 10.3-9.5 |
| Ten Mile Reservation Pond | Pawtucket, R.I. | 6.2-5.8 |
| Central Pond | East Providence, R.I. | 4.6-3.2 |
| Turner Reservoir | East Providence, R.I. | 3.2-2.5 |

## TABLE 6.3 TEN MILE RIVER FLOW GAGING STATIONS

| Station Number | Location | River Mile |
|---|---|---|
| | **Ten Mile River** | |
| TM02 | Cemetery, off W. Bacon St., North Attleboro | 19.8 |
| TM03 | E. Washington St., N. Attleboro | 18.8 |
| TM06 | Near Cedar St., above N. Attleboro WWTP, N. Attleboro | 15.6 |
| TM11 | Tiffany St., N. Attleboro | 10.7 |
| TM14 | Central Ave., Pawtucket, R.I. | 7.0 |
| | **Bungay River** | |
| BG02 | Holden St., Attleboro | 14.0, 0.6 |
| | **Speedway Brook** | |
| SW01 | S. Main St. (Rt. 152), Attleboro | 11.9, 0.1 |
| | **Seven Mile River** | |
| SM01 | County Road., Attleboro | 7.5, 0.3 |

## TABLE 6.4 TEN MILE RIVER POINT SOURCE DISCHARGE MONITORING

| Discharger | Location | River Mile |
|---|---|---|
| Whiting and Davis | Plainville | 19.9 |
| Hilsinger | Plainville | 19.7 |
| Cook-Horton | North Attleboro | 19.0 |
| Handy and Harmon | North Attleboro | 18.1 |
| Balfour, Plant 2 | North Attleboro | 18.0 |
| C. Ray Randall | North Attleboro | 16.7 |
| B & J Jewelry | North Attleboro | 16.3 |
| N. Attleboro Waste Water Treatment Plant | North Attleboro | 15.4 |
| Walton and Lonsbury | Attleboro | 14.3 |
| Mt. Vernon Silver | Attleboro | 14.0 |
| Balfour, Plant 1 | Attleboro | 13.1 |
| Fostor Metal Products | Attleboro | 12.95 |
| Lambert Anodizing | Attleboro | 12.9 |
| Montrose-Haveson | Attleboro | 12.7 |
| Levens | Attleboro | 12.4 |
| Leach and Garner | Attleboro | 11.9 |
| Robbins Co. | Attleboro | 11.9 |
| Swank, Inc. | Attleboro | 11.9 |
| Handy and Harmon | Attleboro | 10.0 |
| Attleboro Waste Water Treatment Plant | Attleboro | 7.8 |

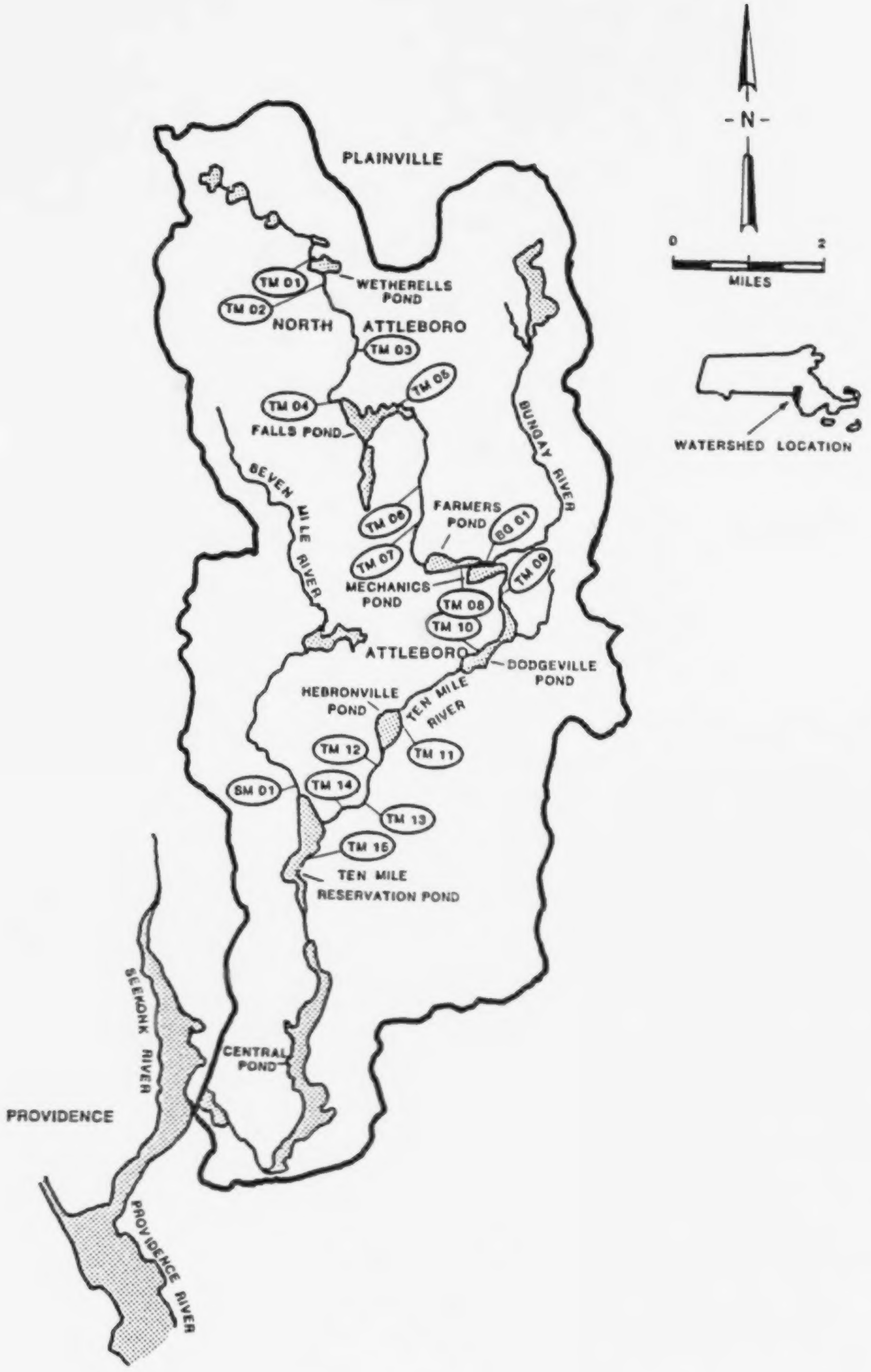

N
0
2
MILES
WATERSHED LOCATION
PLAINVILLE
WETHERELLS POND
TM 01
TM 02
NORTH ATTLEBORO
TM 03
TM 04
TM 05
FALLS POND
SEVEN MILE RIVER
BUNGAY RIVER
TM 06
FARMERS POND
BG 01
TM 07
MECHANICS POND
TM 09
TM 08
TM 10
ATTLEBORO
DODGEVILLE POND
HEBRONVILLE POND
TEN MILE RIVER
TM 12
TM 11
SM 01
TM 14
TM 13
TM 15
TEN MILE RESERVATION POND
SEEKONK RIVER
CENTRAL POND
PROVIDENCE
PROVIDENCE RIVER

Figure 6.2 Ten Mile River monitoring stations.

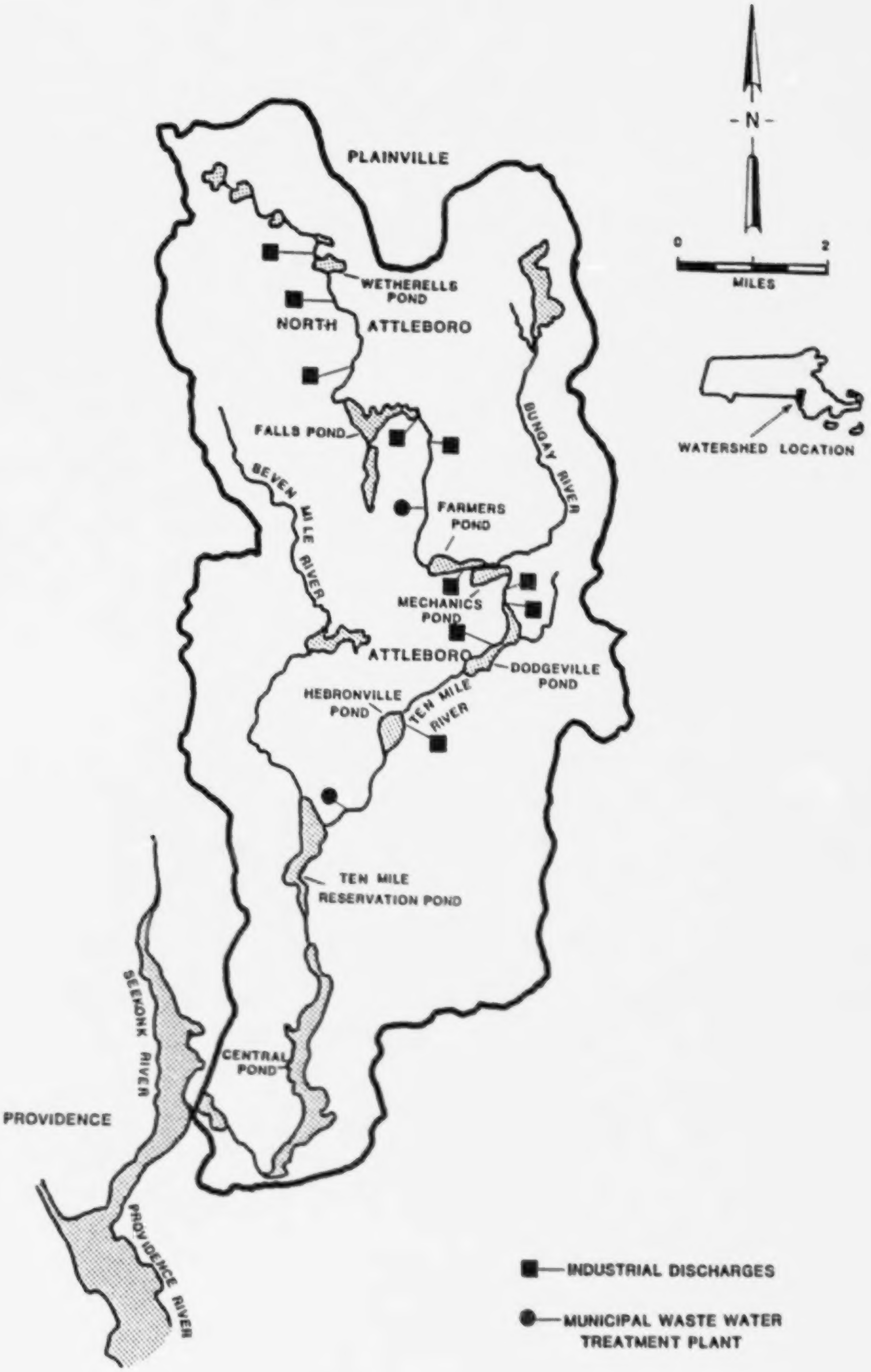

-N-
0
2
MILES
WATERSHED LOCATION
PLAINVILLE
WETHERELLS POND
NORTH ATTLEBORO
FALLS POND
BUNGAY RIVER
SEVEN MILE RIVER
FARMERS POND
MECHANICS POND
ATTLEBORO
DODGEVILLE POND
HEBRONVILLE POND
TEN MILE RIVER
TEN MILE RESERVATION POND
SEEKONK RIVER
CENTRAL POND
PROVIDENCE
PROVIDENCE RIVER
■—INDUSTRIAL DISCHARGES
●—MUNICIPAL WASTE WATER TREATMENT PLANT

Figure 6.3 Ten Mile River point source discharge locations.

the surveys; consequently, they do not represent steady-state conditions. Table 6.5 shows the flows used in this study.

TABLE 6.5 TEN MILE RIVER FLOWS *

| Station | Flow (ft3/s) |
|---|---|
| TM02 | 5.09 |
| TM03 | 7.64 |
| TM06 | 11.95 |
| TM11 | 39.24 |
| TM14 | 77.33 |
| BG02 | 6.79 |
| SM01 | 11.2 + |
| SW01 | 3.0 + |

* Data collected on July 24, 1984

+ Flow estimated from surveys on other dates since data for July 24 were not available.

Time-of-Travel measurements were collected during the 1984 surveys; however, since these data were intended to adjust or "fine-tune" the flows during calibration, they were not used in this study.

Channel depths and widths were measured at the flow stations. Additional data to characterize the channel geometry were also collected at twenty-three cross sections in the 1984 surveys. Since corresponding river miles were not provided, only selected points were used. Impoundment dimensions (depth and surface area) were not available from the 1984 survey; these data were obtained from previous model estimates (DWPC, 1975) and bathymetric maps (DWPC, 1981).

### 6.2.3 Water Quality Data

Chemical concentrations and water quality parameters were measured at river monitoring stations and impoundments on several dates during the 1984 surveys. The parameters available for this application are shown below, and Tables 6.6 and 6.7 list the concentrations at various monitoring stations which were used in this application. Metal loadings data (concentrations and discharge rates) from industrial and municipal point sources were measured in the 1984 surveys. Since only copper loadings were modeled in this application, the data for this metal are shown in Table 6.8. These data represent averages of the data collected during 2-3 separate surveys in July, 1984.

TABLE 6.6 TEN MILE RIVER WATER QUALITY DATA

| River Station | pH | Alkalinity | Hardness | Cl- | $SO_4^{-2}$ | $NO_3$-N | $NH_3$-N | $PO_4$-P | SS |
|---|---|---|---|---|---|---|---|---|---|
| TM01 | 7.2 | 39. | 100. | 17. | 6.0 | 2.2 | 0.06 | 0.03 | 1.5 |
| TM02 | 6.8 | 27. | 71. | 21. | 3.9 | 2.6 | 0.05 | 0.03 | 6.5 |
| TM03 | 6.9 | 26. | 55. | 22. | 3.3 | 1.3 | 0.07 | 0.24 | 12. |
| TM04 | 7.1 | 28. | 52. | 26. | 3.4 | 1.8 | 0.29 | 0.61 | 5.0 |
| TM05 | 7.1 | 23. | 42. | 22. | 2.4 | 0.0 | 0.06 | 0.34 | 5.5 |
| TM06 | 7.2 | 27. | 44. | 21. | 2.2 | 0.9 | 0.07 | 0.34 | 2.0 |
| TM07 | 7.2 | 34. | 50. | 34. | 3.0 | 4.4 | 0.12 | 1.2 | 4.5 |
| TM07A | 7.0 | 28. | 39. | 31. | 2.2 | 2.2 | 0.16 | 0.61 | 5.5 |
| TM08 | 7.1 | 29. | 39. | 67. | 2.2 | 2.7 | 0.11 | 0.43 | 9.0 |
| TM08A | 7.2 | 32. | 42. | 35. | 2.4 | 2.7 | 0.14 | 0.61 | 6.0 |
| TM09 | 7.1 | 30. | 42. | 35. | 2.7 | 3.1 | 0.14 | 0.55 | 7.5 |
| TM10 | 7.1 | 30. | 38. | 32. | 2.4 | 2.7 | 0.12 | 0.61 | 6.0 |
| TM11 | 7.2 | 30. | 38. | 29. | 2.7 | 2.2 | 0.08 | 0.49 | 10. |
| TM12 | 7.1 | 29. | 36. | 27. | 1.8 | 2.2 | 0.05 | 0.37 | 7.0 |
| TM13 | 6.9 | 25. | 38. | 28. | 2.2 | 2.2 | 0.08 | 0.40 | 3.5 |
| TM14 | 7.3 | 33. | 46. | 30. | 2.1 | 7.1 | 0.10 | 0.89 | 4.0 |

## TABLE 6.7 TEN MILE RIVER METAL DATA

| Station | Fe D | Fe T | Cu D | Cu T | Cd D | Cd T | Pb D | Pb T | Ni D | Ni T | Zn D | Zn T |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| TM01 | 0.02 | 0.16 | 0. | 0.47 | 0. | 0.01 | 0.02 | 0.01 | 0.04 | 0.04 | 0.04 | 0.13 |
| TM02 | 0.06 | 0.25 | 0. | 0.08 | 0. | 0. | 0. | 0. | 0.02 | 0.03 | 0. | 0.06 |
| TM03 | 0.14 | 0.84 | 0.02 | 0.05 | 0. | 0.01 | 0. | 0. | 0.02 | 0.03 | 0. | 0.01 |
| TM04 | 0.30 | 1.0 | 0.02 | 0.03 | 0.04 | 0.01 | 0.01 | 0. | 0.05 | 0.06 | 0. | 0.03 |
| TM05 | 0.09 | 0.29 | 0.01 | 0.15 | 0. | 0. | 0.08 | 0. | 0.03 | 0.04 | 0. | 0.05 |
| TM06 | 0.22 | 0.43 | 0.02 | 0.02 | 0.01 | 0. | 0.08 | 0.01 | 0.05 | 0.06 | 0. | 0.01 |
| TM07 | 0.18 | 0.35 | 0.01 | 0.03 | 0. | 0. | 0. | 0.04 | 0.05 | 0.04 | 0.01 | 0.01 |
| TM07A | 0.40 | 0.76 | 0.01 | 0.01 | 0.02 | 0. | 0. | 0.03 | 0.01 | 0.04 | 0. | 0. |
| TM08 | 0.40 | 0.72 | 0.01 | 0.04 | 0.01 | 0. | 0.01 | 0.04 | 0.01 | 0.05 | 0. | 0. |
| TM08A | 0.44 | 0.83 | 0.02 | 0.01 | 0.01 | 0. | 0.03 | 0. | 0.10 | 0.10 | 0.05 | 0.03 |
| TM09 | 0.41 | 0.85 | 0.02 | 0.02 | 0. | 0. | 0.02 | 0. | 0.10 | 0.10 | 0.03 | 0.03 |
| TM10 | 0.42 | 0.79 | 0.01 | 0.02 | 0.01 | 0. | 0.01 | 0. | 0.09 | 0.09 | 0.03 | 0.03 |
| TM11 | 0.51 | 0.89 | 0.02 | 0.02 | 0.01 | 0. | 0. | 0.03 | 0.07 | 0.09 | 0.02 | 0.01 |
| TM12 | 0.52 | 0.87 | 0.02 | 0.03 | 0.03 | 0.01 | 0.05 | 0.10 | 0.07 | 0.08 | 0.03 | 0.06 |
| TM13 | 0.42 | 0.80 | 0.02 | 0.02 | 0.01 | 0. | 0.03 | 0.04 | 0.11 | 0.09 | 0.0 | 0.01 |
| TM14 | 0.46 | 0.79 | 0.02 | 0.02 | 0.02 | 0.01 | 0.03 | 0.08 | 0.03 | 0.08 | 0.03 | 0.03 |
| Wetherells Pond | | | | | | | | | | | | |
| WC | 0.10 | 1.1 | 0. | 0.07 | 0. | 0. | 0. | 0.03 | 0.04 | 0.04 | 0.01 | 0.01 |
| B | - | 375. | - | 1000. | - | 195. | - | 40. | - | 650. | 0 | 750. |
| Falls Pond | | | | | | | | | | | | |
| WC | 0.16 | 0.38 | 0.02 | 0.06 | 0. | 0. | 0.04 | 0.04 | 0.05 | 0.07 | 0.04 | 0.03 |
| B | - | 170. | - | 850. | - | 17. | - | 105. | - | 190. | - | 1000. |
| Farmers Pond | | | | | | | | | | | | |
| WC | 0.24 | 0.40 | 0. | 0.11 | 0. | 0. | 0.05 | 0.06 | 0.04 | 0.09 | 0. | 0.09 |
| B | - | 250. | - | 950. | - | 29. | - | 65. | - | 230. | - | 800. |
| Mechanics Pond | | | | | | | | | | | | |
| WC | 0.30 | 0.65 | 0. | 0. | 0. | 0. | 0.06 | 0.06 | 0.01 | 0.02 | 0. | 0. |
| B | - | 280. | - | 1200. | - | 44. | - | 43. | - | 380. | - | 1000. |
| Dodgeville Pond | | | | | | | | | | | | |
| WC | 0.51 | 0.78 | 0.02 | 0.02 | 0.05 | 0.06 | 0.07 | 0.06 | 0.06 | 0.07 | 0. | 0. |
| B | - | 350. | - | 2150. | - | 175. | - | 70. | - | 1400. | - | 950. |
| Hebronville Pond | | | | | | | | | | | | |
| WC | 0.57 | 0.91 | 0. | 0.01 | 0. | 0. | 0. | 0.01 | 0.09 | 0.09 | 0.02 | 0.02 |
| B | - | 285. | - | 135. | - | 115. | - | 39. | - | 700. | - | 900. |

D = dissolved　T = total　WC = water column, mg/l　B = benthic, mg/kg

## TABLE 6.8 TEN MILE RIVER COPPER LOADINGS - JULY 1984

| Discharger | Flow | Cu (mg/l) |
|---|---|---|
| Whiting & Davis | 7.1E3 | 0.52 |
| Hilsinger | 3. E3 | 0.11 |
| Cook-Horton | 2.0E3 | 0.5 |
| Handy-Harmon | 1.6E4 | 0.91 |
| Balfour, No. 2 | 1.2E4 | 0.78 |
| C. Ray Randle | 8. E3 | 0.90 |
| B. & J. Jewelry | 2.8E3 | 0.22 |
| N. Attelboro WWTP | 4.3E5 | 0.06 |
| Walton & Lonsbury | 5. E3 | 0.07 |
| Bungay River | 6.9E5 | 0.05 |
| Mt. Vernon Silver | 1.6E2 | 0.42 |
| Balfour, No. 1 | 1.6E3 | 0.76 |
| Foster Metal Products | 3. E2 | 2.0 |
| Lambert Anodizing | 3. E1 | 0.04 |
| Levens | 1.6E3 | 9.3 |
| Leach & Gardner | 2.0E3 | 0.46 |
| Swank Inc. | 1.4E4 | 1.1 |
| Speedway Brook | 4. E5* | 0.095 |
| Attleboro WWTP | 9.3E5 | 0.09 |
| Seven Mile River | 1. E6* | 0.0 |

* estimated flow

## CHEMICAL/WATER QUALITY PARAMETERS

### River Stations

pH
alkalinity
hardness
conductivity
Cl-

$SO4^{-2}$
NH3-N
NO3-N
Kjeldahl-N
total PO4

Ortho PO4
suspended solids
total solids
COD
BOD-5

### River Stations And Impoundments

Al (total, dissolved)
Cd
Cr

Cu
Fe
Pb

Ni
Ag
Zn

### 6.2.4 Data Problems

Available data for this study contained problems which limited the scope of the application and the reliability of the model results. Primary among them is the lack of steady-state hydraulic conditions - a crucial requirement of MEXAMS - which existed during the data collection surveys. This and other data problems are documented below to demonstrate data requirements for MEXAMS and to suggest improvements for future data collection efforts in Ten Mile River.

Absence of steady-state conditions was evidenced by significantly decreasing flows over the period of the surveys as well as changes in relative fraction of river flow provided by two major tributaries. Attempts to estimate missing flow data for one survey date based on flows for another date were inconsistent. Fortunately, chemical samples and flow measurements were obtained simultaneously (i.e., same day); however, the variations in both chemical concentrations and flows from one day to the next suggest that conditions on the river were changing rapidly. It is recommended that MEXAMS data collection occur during periods of constant flow.

Hydraulic characterization of the impoundments on Ten Mile River was inadequate, especially since these ponds dominate metal transport, and the pond sediments are large sinks for metals. At a minimum, average depths and surface areas are necessary for EXAMS. Bathymetric maps of the impoundments from the 1981 surveys of the river lacked scale information, and the 1984 surveys did not measure impoundment hydraulics.

Water quality data contained two significant limitations. First, metal concentrations were imprecise due to the analytical methods. The flame atomic adsorption method used by DWPC apparently provided an accuracy of 0.01 mg/l for most metals, which generally resulted in reported concentrations of one significant figure and many dissolved concentrations of 0. Also, dissolved concentrations were greater than total concentrations in many samples. Calibration of MEXAMS in Ten Mile River requires metal concentration measurements accurate to 0.001 mg/l.

A second and related problem was the lack of metal adsorption data for Ten Mile River. MINTEQ adsorption models require precise measurements of dissolved and adsorbed concentrations using native water and sediments, as well as detailed chemical analyses of the samples. It was hoped that the lack of adsorption data could be partially alleviated by using the routine metal concentration data; however, the previously referenced limitations of those data precluded their use.

Measured redox potentials (Eh) were not available. While Eh is generally regarded as a poor indication of the equilibrium state of individual metal couples in a natural system, these data can provide insight into the chemical state of a system. Major cationic species such as $Ca^{+2}$, $Mg^{+2}$, $Na^{+}$, and $K^{+}$, were not determined individually; consequently, ionic strength computations in MINTEQ were inaccurate. Conductivity measurements, from which ionic strength can be estimated, were available.

## 6.3 APPLICATION OF MEXAMS

### 6.3.1 Strategy and Overview

The strategy employed in this application of MEXAMS to Ten Mile River was dictated largely by the available data and associated problems documented in the previous section. Copper speciation and adsorption was simulated in a fifteen mile stretch of the river from the Fuller Pond outlet downstream to Ten Mile Reservation Pond. The EXAMS input was based on flow data of July 24, 1984 and limited channel geometry data. Segmentation of the river generally followed the gross channel morphology, i.e. impoundments and intervening channel sections formed the segments. Fifteen segments or thirty EXAMS compartments were delineated and divided into three sets of ten compartments since MEXAMS is limited to ten compartments per run. A complete Ten Mile River simulation required three successive model runs, with simulated metal outflow from the downstream end of one run providing the input loading to the upstream end of the next run.

MINTEQ input was developed based on the water chemical survey data of July 24, 1984 and mean copper loadings from three July 1984 dates. Each EXAMS compartment requires an associated MINTEQ input set; however, in order to minimize computation and because many of the chemical constituent concentrations exhibited little spatial variation, several EXAMS compartments were assigned the same MINTEQ input set. For example, all channel water column and benthic compartments in each ten-compartment section were assigned the same MINTEQ input. Also, several ionic species were omitted from the final MINTEQ input since they are unlikely to form complexes with metals, or to impact the equilibrium calculation significantly. The species omitted were $Cl^-$, $NO_3^-$, $PO_4^{-3}$, $Na^+$, $K^+$, and $NH_4^+$.

The adsorption model selected was activity Kd. Extensive data requirements of other MINTEQ adsorption models precluded their use; and in fact, the available data were inadequate for reliable application of the activity Kd model. To demonstrate the application process of this model, preliminary MINTEQ runs were performed to determine the activity Kd coefficients for copper under different conditions of water chemistry and sediment concentration. These Kd's were subsequently used in the MEXAMS simulation

### 6.3.2 Exams Input

This section presents a line-by-line description of the EXAMS input shown in Tables 6.9 and 6.10. It includes discussion of how various input values were determined for this application. It should be noted that line numbers shown in Tables 6.9 and 6.10 apply to this application only; they are not uniquely associated with the input data type in this example. EXAMS input for MEXAMS applications consists of two separate input files, one which describes the compartmentalization of the ecosystem, compartment connectivities, flows, etc; and another which specifies the metal loadings to the ecosystem compartments.

Compartmentalization

The file (Table 6.9) containing compartmental information, flows, etc. begins with two lines of alphanumeric, descriptive data which may be used by the modeler to identify the application. Line 3 contains model flags which should all be zero (blank line) for metals applications. Lines 4 and 5 are again descriptive information. The next line (6) specifies

## TABLE 6.9 EXAMS INPUT - GENERAL DATA

```
Line

   1        HVM
   2        Copper
   3        0 0 0 0 0
   4        TMR
   5        TEN MILE RIVER EXAMS INPUT - SECTION I, REACHES 1-10
   6           10
   7        L
   8        B
   9        L
  10        B
  11        L
  12        B
  13        L
  14        B
  15        L
  16        B
  17         40.00
  18               0.5       0.0       0.5       0.0       0.5       0.0       0.5       0.0
                   0.5       0.0
  19             2200.      333.     1600.       80.     3800.      710.    46000.     1150.
                 2900.      570.
  20             6670.     6670.     1600.     1600.    14200.    14200.    23000.    23000.
                11400.    11400.
  21              0.33      0.05       1.0      0.05       .27      0.05       2.0      0.05
                  0.25      0.05
  22              520.       0.0       3.0       0.0       30.       0.0       0.0       0.0
                   11.       0.0
  23               2.6       0.0       .01       0.0       .15       0.0       0.0       0.0
                   .05       0.0
  24               0.0       0.0       30.       0.0      215.       0.0      215.       0.0
                  205.       0.0
  25               0.0       0.0       .15       0.0       1.1       0.0       1.1       0.0
                   1.0       0.0
  26               0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0
                   0.0       0.0
  27         100.0
  28         5.000
  29        0.8910E+110.3380E+120.1110E+130.2990E+130.5400E+130.8840E+130.1380E+140.1850E+14
  30        0.2330E+140.2810E+140.5210E+140.1810E+150.2110E+150.2260E+150.2410E+150.2680E+15
  31        0.2940E+150.3660E+150.5260E+150.6920E+150.7120E+150.6880E+150.8140E+150.9170E+15
  32        0.9270E+150.9590E+150.9830E+150.9300E+150.9490E+150.1000E+160.1050E+160.1060E+16
  33        0.1070E+160.1080E+160.1080E+160.1080E+160.1070E+160.1030E+160.9880E+15
  34             1.190       0.0     1.190       0.0     1.190       0.0     1.190       0.0
                 1.190       0.0
  35              100.       0.0      100.       0.0      100.       0.0      100.       0.0
                  100.       0.0
  36               4.0      1.85       2.0      1.85       12.      1.85       2.0      1.85
                   4.0      1.85
  37               0.0      137.       0.0      137.       0.0      137.       0.0      137.
                   0.0      137.
```

TABLE 6.9   (CONTINUED)

```
Line

 38        5
 39        1    3    5    7    9
 40        3    5    7    9    0
 41          1.0      1.0       1.0       1.0       1.0
 42        5
 43        1    3    5    7    9
 44        2    4    6    8    10
 45         6670.     1600.    14200.    23000.    11400.
 46          0.15      0.5      0.13       1.0      0.12
 47        1.0E-05   1.0E-05  1.0E-05   1.0E-05   1.0E-05
 48         0.038     0.038    0.038     0.038     0.038     0.038     0.038     0.038
            0.038     0.038
 49          25.       25.       25.       25.       25.       25.       25.       25.
             25.       25.
 50          25.       25.       25.       25.       25.       25.       25.       25.
             25.       25.
 51          22.       22.       22.       22.       22.       22.       22.       22.
             22.       22.
 52          7.2       7.2       7.2       7.2       7.2       7.2       7.2       7.2
             7.2       7.2
 53          6.8       6.8       6.8       6.8       6.8       6.8       6.8       6.8
             6.8       6.8
 54          0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0
             0.0       0.0
 55          1.0       1.0       1.0       1.0       1.0       1.0       1.0       1.0
             1.0       1.0
 56          .01       .01       .01       .01       .01       .01       .01       .01
             .01       .01
 57          20.       20.       20.       20.       20.       20.       20.       20.
             20.       20.
 58          1.0       1.0       1.0       1.0       1.0       1.0       1.0       1.0
             1.0       1.0
 59          .01       .01       .01       .01       .01       .01       .01       .01
             .01       .01
 60           5.       0.0        5.       0.0        5.       0.0        5.       0.0
              5.       0.0
 61           2.       0.0        2.       0.0        2.       0.0        2.       0.0
              2.       0.0
 62          10.       0.0       10.       0.0       10.       0.0       10.       0.0
             10.       0.0
 63          0.0       0.0       0.0       0.0       0.0       0.0       0.0       0.0
             0.0       0.0
 64        2
 65        3    7    0    0    0
 66        4    8    0    0    0
 67          0.05      0.05      0.0       0.0       0.0
 68          0.0       0.0       0.0       0.0       0.0
 69         1600.    23000.      0.0       0.0       0.0
```

TABLE 6.10 EXAMS INPUT - METAL LOADING

```
Line

  1        HVM
  2        TMR
  3            4
  4            1     0.243        0.         0.0        0.0        0.0
  5            3    0.0003        0.         0.0        0.0        0.0
  6            5    0.0253        0.         0.0        0.0        0.0
  7            9    0.0076        0.         0.0        0.0        0.0
```

the number of EXAMS compartments to be modeled, and lines 7-16 are the respective compartment types.

Ten Mile River was divided into fifteen river segments based on the locations of major inflows, impoundments, and other significant changes in channel hydraulics. The information necessary to segment the river was obtained from previous modeling study documentation and descriptions of past and current river surveys conducted by DWPC (see Section 6.2). Table 6.11 lists the segments, mile points, and other pertinent data, and Figure 6.4 shows where reach boundaries occur. The river section immediately downstream of Fuller Pond was selected as the first segment due to the location of the first sampling station, and the lack of significant waste discharge upstream of this section.

Generally, the segmentation followed the gross channel geometry with each impoundment forming a segment and each of the channels connecting two impoundments forming a segment. Significant tributary inflows (Bungay River and Seven Mile River) and waste discharge volumes (wastewater treatment plants) also served as segment dividing points. Refinement of this segmentation should more closely consider the locations of significant metal loadings and river sampling stations. Since MEXAMS compartments are completely mixed, actual loading near the downstream end of a segment is treated identically to upstream loading; consequently, misleading concentrations may be predicted in such cases. The ten compartments shown in Table 6.9 represent the five upstream river segments modeled in Ten Mile River. Each segment consists of a littoral (water column) and an underlying benthic (sediment) compartment. Lines 7-16 specify the compartment types in downstream order with L designating littoral and B for benthic.

Line 17 is the latitude of the basin and line 18 contains the mean wind velocity (m/s) over each compartment. Lines 19-21 consist of the compartment dimensions: volume (m3), surface area (m2), and depth (m). These data were obtained from the 1984 and previous river survey data described in Section 6.2. Benthic compartments were all assigned depths of 5 cm; and surface areas were the same as the overlying water column compartment.

Lines 22-23 contain the streamflow (m3/hr) entering each compartment and associated sediment load (kg/hr). These loadings represent inflow from reaches and sources that are not part of the simulated ecosystem, such as waste flows, tributary flows, and inflow to the upstream end of the system. The flows were obtained by compiling a complete budget of the ecosystem starting with the recorded flows at various points along the river and recorded waste and tributary inflows. It was assumed that no gains or losses occurred from rainfall,

## TABLE 6.11 TEN MILE RIVER SEGMENTATION

| Compartment No. | Upstream Mile | Downstream Mile | Comments/Descriptions |
|---|---|---|---|
| 1,2 | 20.7 | 19.8 | Outlet of Fuller Pond to inlet of Wetherells Pond; |
| 3,4 | 19.8 | 19.6 | Inlet to outlet of Wetherells Pond (dam); |
| 5,6 | 19.6 | 17.4 | Outlet of Wetherells Pond to inlet of Falls Pond; |
| 7,8 | 17.4 | 16.7 | Inlet to outlet of Falls Pond (dam); |
| 9,10 | 16.7 | 15.25 | Outlet of Falls Pond to North Attleboro WWTP; |
| 11,12 | 15.25 | 14.5 | North Attleboro WWTP to inlet of Farmers Pond; |
| 13,14 | 14.5 | 14.3 | Inlet to outlet of Farmers Pond; |
| 15,16 | 14.3 | 13.4 | Outlet of Farmers Pond to outlet of Mechanics Pond (dam); Bungay River confluence |
| 17,18 | 13.4 | 12.3 | Outlet of Mechanics Pond to inlet of Dodgeville Pond; |
| 19,20 | 12.3 | 11.2 | Inlet to outlet of Dodgeville Pond (dam); Speedway Brook confluence; |
| 21,22 | 11.2 | 10.3 | Outlet of Dodgeville Pond to inlet of Hebronville Pond; |
| 23,24 | 10.3 | 9.5 | Inlet to outlet of Hebronville Pond; (dam) |
| 25,26 | 9.5 | 8.45 | Outlet of Hebronville Pond to AD&F Dam; |
| 27,28 | 8.45 | 7.75 | AD&F Dan to Attleboro WWTP Seven Mile River Confluence; |
| 29,30 | 7.75 | 6.2 | Attleboro WWTP to inlet of Ten Mile Reservation Pond; (Seven Mile River and WWTP flows) |

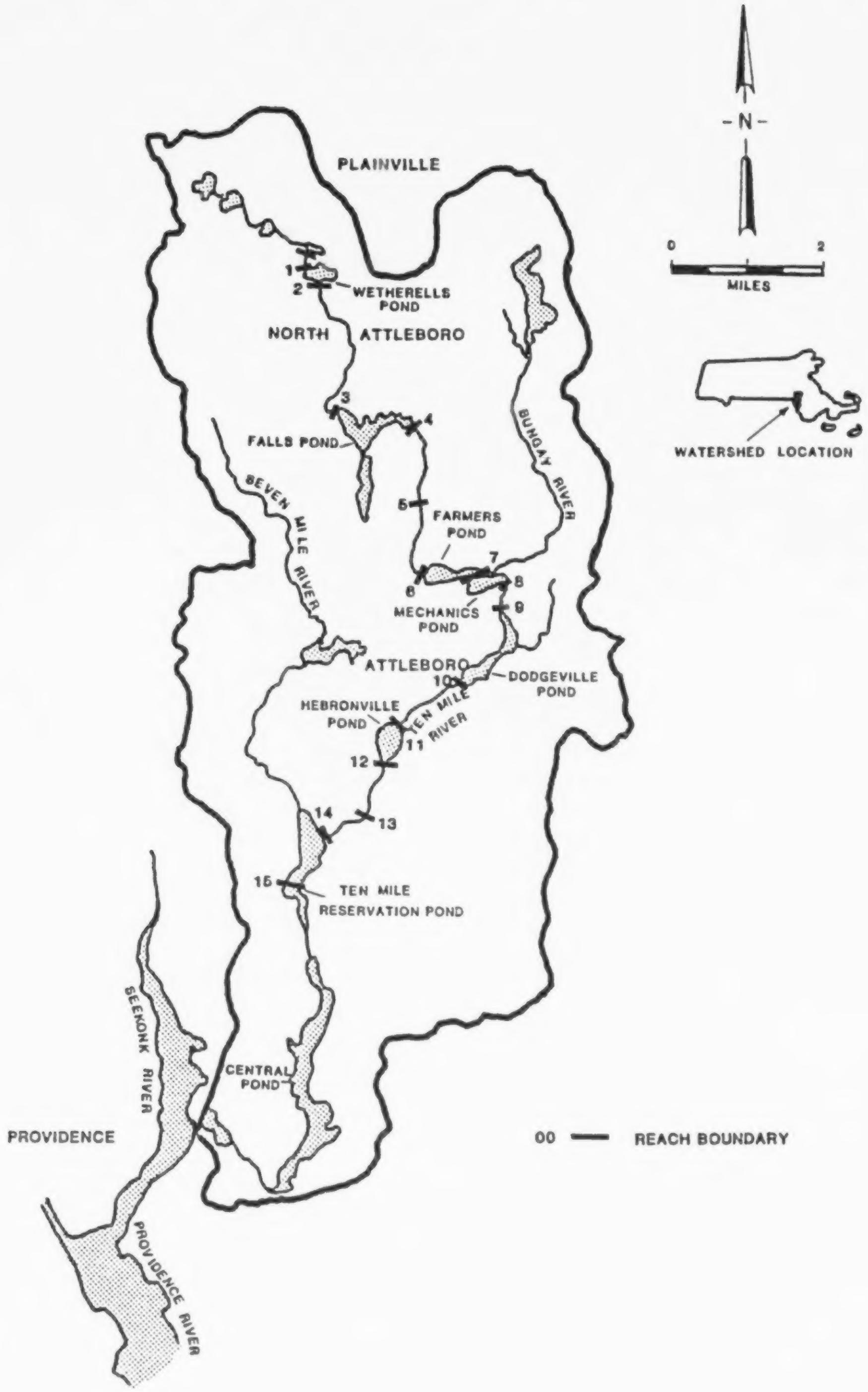

N
0
2
MILES
WATERSHED LOCATION
PLAINVILLE
1
2
WETHERELLS POND
NORTH ATTLEBORO
3
4
FALLS POND
BUNGAY RIVER
SEVEN MILE RIVER
5
FARMERS POND
7
6
8
MECHANICS POND
9
ATTLEBORO
10
DODGEVILLE POND
HEBRONVILLE POND
TEN MILE RIVER
11
12
14
13
15
TEN MILE RESERVATION POND
SEEKONK RIVER
CENTRAL POND
PROVIDENCE
00 REACH BOUNDARY
PROVIDENCE RIVER

Figure 6.4 Ten Mile River Basin reach boundaries.

evaporation, or interflow (line 26). Moving downstream, all deficiencies in the flow at a recording station were made up by nonpoint runoff from the land tributary to the river between the previous flow recording station and the current one. This runoff (shown in line 24) was distributed uniformly to EXAMS water column compartments based on relative tributary area. Sediment load (lines 23 and 25) entering a compartment was obtained by simply assuming that the entering flow - both nonpoint and point sources - contain sediment at the observed sediment concentration of the river. This was done only for consistency since EXAMS does not compute a mass balance on sediment. Sediment loadings have no effect on EXAMS computations; sediment transport in EXAMS is based entirely on the user-input sediment concentrations in the compartments.

Lines 27 and 28 are monthly rainfall (mm/mo) and cloud cover (tenths). Lines 29-34 are not used for MEXAMS, but must exist in the input. Line 35 contains compartment evaporation rates (mm/mo). In this application, rainfall and evaporation are assumed to result in no net gain or loss to the system. They were arbitrarily assigned the values shown. Lines 36 and 37 characterize the sediment concentrations in the river. Line 36 contains the sediment concentrations (mg/l) for water column compartments and bulk density (g/cm3) for benthic compartments. The water column values were obtained from the recorded survey data, and the benthic values were assumed to be 1.85 g/cm3. Line 37 contains a parameter (PCTWA) which is a measure of the porosity or the percent of water in a benthic compartment, and is defined as 100 * fresh weight/dry weight of sediment. A value of 137 was assumed for the Ten Mile River.

Lines 38-41, 42-47, and 64-69 define the connectivity of the ecosystem compartments with regard to advection, dispersion, and sediment settling, respectively. (Note, lines 48-63 are not used for MEXAMS, but must exist in the input.) The first line in each of the sets gives the number of compartment connections of that type, and the next two lines contain the source and receiving compartment numbers. The input shown in Table 6.9 defines advective flows occurring between adjacent water column compartments in the configuration shown in the upper portion of Figure 6.5. For each compartment pair, line 41 contains the corresponding fraction of advective flow (exitting from a compartment) that enters the target compartment.

Dispersive flows are assumed to occur only between water column and the underlying benthic compartment as shown in Figure 6.5. Line 45 contains the cross-sectional area (m2) over which the dispersive flow occurs. The river segment's surface area was used for this area. Line 46 contains the characteristic length (m) for the dispersive flow. This may

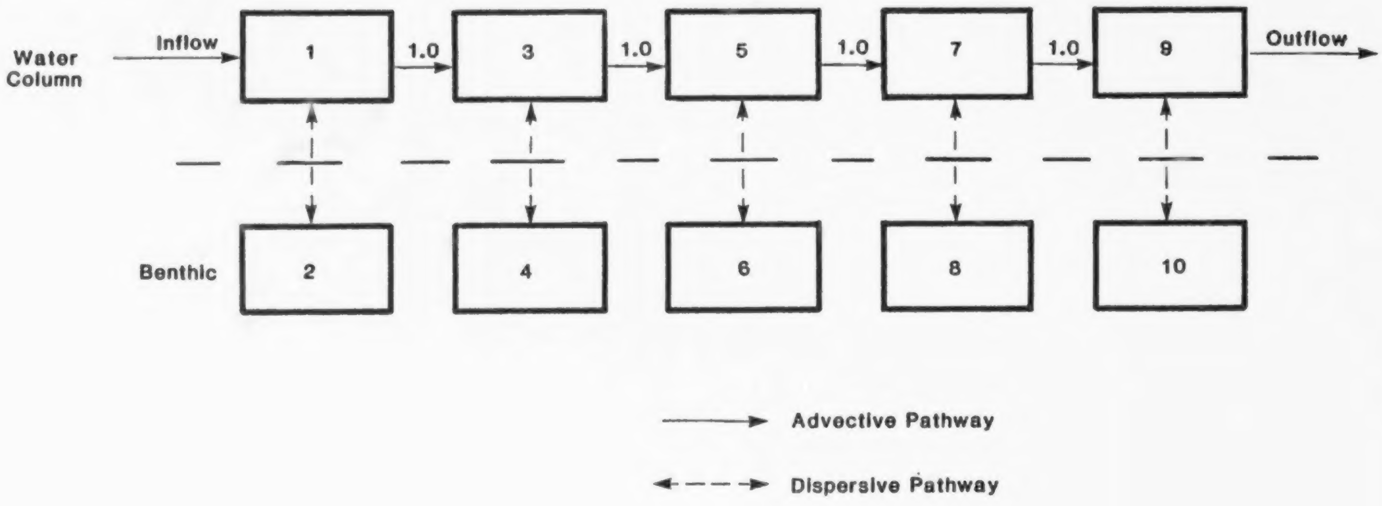

Water Column
Inflow
1
1.0
3
1.0
5
1.0
7
1.0
9
Outflow
Benthic
2
4
6
8
10
Advective Pathway
Dispersive Pathway

Figure 6.5 Ten Mile River Compartment Configuration.

be estimated as the average depth of the two compartments. Line 47 contains the corresponding dispersion coefficients (m2/hr), which are primarily a function of physical mixing processes across the water-sediment interface and diffusion of the chemical in the interstitial water. This parameter is important in determining the relative distribution of metal between sediment and water column. Lines 67-69 contain the sediment settling rate (m/hr), rate of sediment resuspension (mm/yr), and cross sectional area (m2) for settling/resuspension calculations. No data were available to select these parameters.

Metal Loads

The file (Table 6.10) containing metal loads begins with two lines of descriptive information. Line 3 is the number of compartments receiving external metal loadings, i.e., metal that is not the result of outflow from other ecosystem compartments. Lines 4-7 are the loading rates for these compartments in kg/hr. The first field in these lines is the compartment number, and the next five fields are the loadings from streamflow, rainfall, interflow, nonpoint source flow, and drift. For Ten Mile River, metal loadings were all assumed to occur via streamflow (waste effluent and tributary flow) into water column compartments. The loadings were computed from the loading rates (concentration * flow) for each of the measured discharges for the July, 1984 survey. Table 6.8 lists the averaged flows and copper concentrations along with the corresponding dischargers, and Figure 6.3 indicates the locations of point-source discharges along the river. All such loading rates for a particular river segment were summed to obtain the loading rate for the corresponding EXAMS water column compartment.

### 6.3.3 MINTEQ Input

Twelve separate MINTEQ input files were used to represent the water chemistry of the 30 EXAMS compartments modeled in Ten Mile River. Each MINTEQ file is identical in overall structure and options. Differences occur in the concentrations of chemical components at different locations in the system; Also, the adsorption coefficients for pond water column compartments are different than benthic compartments. This section documents a typical MINTEQ input file for this application and the rationale for the various MINTEQ files representing the first five river segments (ten compartments). Table 6.12 shows the MINTEQ file, where the line numbers refer to this file only; they are not uniquely associated with the input data type in this example.

## TABLE 6.12 MINTEQ INPUT

```
Line

  1      TEN MILE RIVER MINTEQ INPUT - CU IN RIVER SECTION I
  2      JULY 24 1984 - CHANNELS (WATER COLUMN AND SEDIMENTS)
  3      25.00 MG/L    0.00
  4      1 0 1 1 2 0 0 0
  5      1   0.00   0.00   0.00   0.00
  6          140 2.800E+01   0.00                    CO3 (alk.)
  7          330 0.000E+01  -7.05                    H+
  8          732 3.500E+00   0.00                    SO4
  9          150 1.300E+01   0.00                    Ca
 10          460 2.000E+00   0.00                    Mg
 11          280 1.400E-01   0.00                    Fe
 12          600 3.000E-02   0.00                    Pb
 13          540 3.000E-02   0.00                    Ni
 14          231 0.000E-00   0.00                    Cu
 15          950 1.000E-02   0.00                    Zn
 16          990 0.000E-00   0.00                    SOH1
 17
 18        3   2
 19          330 7.050E+00   0.00
 20          990 0.000E+00   0.00
 21
 22        2   1
 23      9902310 SOH-CU                  1.1388
 24                1.00 231    1.00 990
 25
 26
```

The MINTEQ input file is divided into three sections which are separated by blank lines. Section 1, the Basic Input, defines run-specific options, adsorption data, and the basic water chemistry analysis data. Lines 1 and 2 contain descriptive information for the run. Line 3 contains the water temperature (C) and the name of the units which will be used to input the chemical concentration data. The '0.0' in Line 3 indicates that the ionic strength of the system is not fixed at a constant value, but is computed by the program. Line 4 contains run-specific option flags. In the input file shown, the options selected are itemized and, where necessary, explained below:

1) Inorganic carbon is input as 'total alkalinity' since this quantity was measured and available.

2) Debug output is not generated.

3) Execution continues regardless of computation of an initial charge imbalance. An initial charge imbalance is expected since a number of ionic species were omitted from the system to minimize computation and output of unimportant chemical species.

4) All solids are permitted to precipitate since we did not know which solids would be significant, and we did not want to eliminate any important ones. Subsequent simulations should be modified to limit the solids to those in Table 7 of the MEXAMS User's Guide.

5) The iterations are limited to 100.

6) The pH is not permitted to vary due to precipitation/dissolution of solids. The pH was a measured quantity, and was not expected to be affected by chemical precipitation in this system.

7) The ionic strength is computed by the program. Since several significant ionic species were omitted from the system, the computed ionic strength may not be representative of true conditions. A better alternative is to fix the ionic strength at a value estimated from available data such as conductivity.

Line 5 contains a flag designating the particular adsorption model being used (activity Kd) and four parameters, none of which are required for this model. Lines 6-16 are the component input lines, each containing a number identifying the chemical component and its observed concentration. The third field shown in these lines allows the user to input either an initial guess for the component's activity (log) or the actual fixed activity for components which have been designated Type III. In Table 6.12, the components'chemical formulae have been included for this discussion; they are not read by the program.

Several additional ionic species which were observed or are likely present in significant concentrations were omitted. These species, which include $Na^+$, $K^+$, $NH_4^+$, $Cl^-$, $NO_3^-$, and $PO_4^{-3}$, do not participate in the formation of most significant aqueous complexes in aquatic systems, and their omission minimized the computational requirements for this application. An initial MINTEQ simulation that included these species confirmed this point.

The component concentrations in Table 6.12 were estimated by averaging the analytical data for the water quality stations located on the upper channel sections of the river. All metal concentrations are the observed dissolved concentrations except the "metal being followed", which is input as 0. This quantity is computed by MEXAMS based on loading. Carbonate ($CO_3^{-2}$) is actually the total alkalinity value. Since the activity of H+ is known (observed pH), its analytical concentration is input as 0, and its activity (log) is input. The solid or adsorbent (SOH1) is input with a concentration of 0; however, it automatically is assigned an activity of 1 because the activity Kd model is being used.

Section 2 of the MINTEQ input contains the species type changes for the run. As indicated in Line 18, two species are changed in this application, and they are both changed to Type III ("fixed") species. Lines 19 and 20 contain the species ID numbers and new log K value for the two species, H+ and SOH1. H+ activity is fixed at the value given by the measured pH, and the solid is assumed to be in infinite supply. Subsequent simulations should also change a number of solid species to Type V, i.e. "dissolved solids subject to precipitation." This would limit the considered solids to those likely to form kinetically, and would conversely prevent formation (predicted) of solids which are unlikely.

Section 3 of the input contains new species which are added to the database for this application. Line 22 indicates that one species of Type II is added. The user must explicitly specify adsorption reactions for any adsorption model used. Line 23 contains a species ID number for the new solid-Cu complex, its name, and the equilibrium constant (log), which is the activity Kd. Line 24 contains the stoiciometric coefficients and corresponding species ID numbers for the adsorption reaction.

The activity Kd model is defined in terms of the activity of uncomplexed metal as opposed to the total dissolved metal concentration. This assumes that only free (uncomplexed) metal adsorbs. Thus, in order to obtain an activity Kd coefficient applicable to a specific water sample, one must have "measurements" of this activity. Analytical techniques measure the dissolved metal concentration which includes uncomplexed metal plus aqueous complexes. To obtain the activity of the metal, separate, preliminary MINTEQ runs were performed on the water analyses used in this application. The activity of uncomplexed metal computed by MINTEQ in these runs was combined with the corresponding measured concentration of adsorbed metal to obtain the activity Kd for each water sample. The activity of the uncomplexed metal is affected by the total ionic composition of the water as well as competition with complexes; consequently, a complete water analysis is necessary to develop the MINTEQ input. Table 6.13 shows the MINTEQ input for determination of the activity Kd for copper in the water column of the first ten-compartment section of Ten Mile River. Note that the input does not include adsorption options and data, and also includes a more detailed water chemistry matrix.

### 6.3.4 EXAMS Output

The EXAMS output is presented in the form of sixteen tables, each containing a particular type of information for all compartments in the ecosystem. The tables are generally self-explanatory and well documented in the EXAMS User's Guide. Tables numbered 2 through 8 describe the EXAMS input in detail. These tables are printed once, during the initial EXAMS computation when the metal is assumed to be all in aqueous form. Tables 9-14 contain the results of EXAMS steady-state computations, and are printed at each EXAMS/MINTEQ iteration, i.e., each time EXAMS calls MINTEQ to recalculate the steady-state concentrations. As stated above, the contents of these tables are self-documented. The reader is directed to the "final" Table 13 which contains the principal EXAMS results, the complete distribution of metal at steady-state in each compartment. This distribution includes the total dissolved (sum of all dissolved forms), adsorbed, and precipitated concentrations in each compartment. Table 6.14 is an example of EXAMS Table 13.

Tables 15 - 17 are printed only at the last EXAMS/MINTEQ iteration, and contain the detailed results of a persistence calculation or the response of the system over time after loading ceases. Also included in these tables is a brief exposure analysis summary of the final steady-state and persistence results.

TABLE 6.13 MINTEQ INPUT FOR COMPUTING ACTIVITY Kd COEFFICIENT

```
TEN MILE RIVER MINTEQ INPUT - CU KD IN WATER COLUMN
JULY 24 1984
25.00 MG/L    0.00
1 0 1 1 2 0 0 0
0   0.00   0.00   0.00   0.00
    140 2.800E+01   0.00                  CO3 (alk.)
    330 0.000E+01  -7.05                  H+
    732 3.500E+00   0.00                  SO4
    150 1.300E+01   0.00                  Ca
    460 2.000E+00   0.00                  Mg
    280 1.400E-01   0.00                  Fe
    600 3.000E-02   0.00                  Pb
    540 3.000E-02   0.00                  Ni
    231 2.333E-02   0.00                  Cu
    950 1.000E-02   0.00                  Zn
    492 8.000E+00   0.00                  NO3-
    580 7.000E-01   0.00                  PO4
    180 2.200E+01   0.00                  Cl-
    500 2.000E+01   0.00                  NA+
    410 1.000E+00   0.00                  K+
    490 7.000E-02   0.00                  NH4+

  3   1
    330 7.050E+00   0.00
```

TABLE 6.14 EXAMS OUTPUT - (TABLE 13)

```
----------------------------------------------------------------------------------
TABLE 13. DISTRIBUTION OF CHEMICAL AT STEADY STATE: IN THE WATER COLUMN:
----------------------------------------------------------------------------------
COMP STEADY-STATE RESIDENT MASS     ********* TOXICANT CONCENTRATIONS *********
 #      2                             TOTAL   DISSOLVED SORBED BY SORBED BY PRECIP TO
                                                          BIOTA   SEDIMENTS SEDIMENTS
     G/M        KILOS          %       MG/*      MG/L      UG/G     MG/KG      MG/L
--- ------      ------      ------  --------- --------- --------- --------- ---------
  1  .154       1.028        6.48   .467       .145      .0        7.23E+04  3.31E-02
  3  .440       .7039        4.44   .440       .145      .0        1.45E+05  5.76E-03
  5  9.01E-02   1.279        8.06   .337       .112      .0        1.87E+04  .0
  7  .530       12.20       76.90   .265       8.83E-02  .0        8.84E+04  .0
  9  5.72E-02   .6517        4.11   .225       7.48E-02  .0        3.75E+04  .0
 SUBTOTAL:      15.86        2.14
 AND IN THE BOTTOM SEDIMENTS:
  2  1.17E-02  7.777E-02     0.01   .173       .145      .0        .107      3.31E-02
  4  46.2       73.88       10.21   684.       .145      .0        684.      .0
  6  8.41E-03   .1194        0.02   .125       .112      .0        8.32E-02  .0
  8  28.2       649.6       89.76   418.       8.83E-02  .0        418.      .0
 10  5.61E-03  6.400E-02     0.01   8.32E-02   7.48E-02  .0        5.55E-02  .0
 SUBTOTAL:      723.7       97.86
TOTAL MASS (KILOGRAMS) =      739.6
----------------------------------------------------------------------------------
```

### 6.3.5 MINTEQ Output

The full MINTEQ output consists of a detailed description of the speciation, sorption, and precipitation in each compartment MINTEQ solves. The output is divided into sections which are printed depending on user-specified options. The output is described in Section 6 of the MEXAMS User's Guide and will not be repeated here. For typical applications of MEXAMS, the most useful output is the "percentage distribution of components" shown in Table 6.15 and the "mass of dissolved, precipitated and adsorbed components" shown in Table 6.16. The final iteration of this output for each compartment provides the results necessary to calibrate MEXAMS and to describe the simulated speciation occurring in the system.

### 6.3.6 MISP Output

The MISP output consists of summary information for the EXAMS-MINTEQ interaction. Dissolved, adsorbed, and precipitated concentrations (mg/l) of the "metal being followed" are printed for all compartments after each computation by EXAMS and MINTEQ except the final EXAMS computation. This information shows the effect of the MINTEQ calculations and can be used to quickly evaluate whether the system has reached steady-state with respect to the EXAMS-MINTEQ iteration scheme.

### 6.3.7 Model Results and Discussion

MEXAMS was executed using the input described above in Tables 6.9, 6.10, and 6.12. It should be noted that calibration of MEXAMS was not performed in this study due largely to the non-steady-state conditions exhibited in the 1984 survey data and lack of critical adsorption and metal concentration data. However, it is instructive to examine the results of the simulation to suggest further data collection and modeling efforts. In Table 6.17, simulated copper concentrations in all water column compartments and impoundment benthic compartments of the first ten-compartment section of Ten Mile River are compared with observed concentrations. As was noted previously, the MINTEQ input for channel benthic compartments was not differentiated from the overlying water column since channel sediments were not sampled, and impoundment sediments were judged to be more significant in transport/fate of metals.

TABLE 6.15 MINTEQ OUTPUT - PERCENTAGE DISTRIBUTION OF COMPONENTS

```
 PERCENTAGE DISTRIBUTION OF COMPONENTS
 STEADY-STATE CONCENTRATIONS FROM EXAMS, COMPUTATION NO. 2
 EXAMS COMPARTMENT NO.  1

CO3
          16.0     PERCENT BOUND IN SPECIES #3301401   KH2CO3 AQ
          83.5     PERCENT BOUND IN SPECIES #3301400   KHCO3 -

ZN
          83.9     PERCENT BOUND IN SPECIES #    950   ZN
           7.8     PERCENT BOUND IN SPECIES #9501400   KZNHCO3 +
           6.7     PERCENT BOUND IN SPECIES #9501401   KZNCO3 AQ

SO4
          94.5     PERCENT BOUND IN SPECIES #    732   SO4
           4.4     PERCENT BOUND IN SPECIES #1507320   KCASO4 AQ

CA
          98.6     PERCENT BOUND IN SPECIES #    150   CA

MG
          98.6     PERCENT BOUND IN SPECIES #    460   MG

FE+2
          99.2     PERCENT BOUND IN SPECIES #    280   FE+2

PB
          11.5     PERCENT BOUND IN SPECIES #    600   PB
           2.2     PERCENT BOUND IN SPECIES #6003300   KPBOH +
          79.3     PERCENT BOUND IN SPECIES #6001401   KPBCO3 AQ
           6.7     PERCENT BOUND IN SPECIES #6001402   KPBHCO3 +

NI
          24.7     PERCENT BOUND IN SPECIES #    540   NI
           2.7     PERCENT BOUND IN SPECIES #5401400   KNIHCO3 +
          72.4     PERCENT BOUND IN SPECIES #5401401   KNICO3 AQ

CU+2
           5.7     PERCENT BOUND IN SPECIES #    231   CU+2
          66.7     PERCENT BOUND IN SPECIES #9902310   SOH-CU
          12.2     PERCENT BOUND IN SPECIES #2311400   KCUCO3 AQ
          12.7     PERCENT BOUND IN SPECIES #2313301   KCU(OH)2 AQ
           2.1     PERCENT BOUND IN SPECIES #2311402   KCUHCO3 +

H
          27.6     PERCENT BOUND IN SPECIES #3301401   KH2CO3 AQ
          72.2     PERCENT BOUND IN SPECIES #3301400   KHCO3 -

SOH1

H2O
           6.1     PERCENT BOUND IN SPECIES #3300020   K OH-
           2.0     PERCENT BOUND IN SPECIES #2313300   KCUOH +
          91.0     PERCENT BOUND IN SPECIES #2313301   KCU(OH)2 AQ
```

TABLE 6.16 MINTEQ OUTPUT - MASS OF DISSOLVED, PRECIPITATED, AND ADSORBED COMPONENTS

```
STEADY-STATE CONCENTRATIONS FROM EXAMS, COMPUTATION NO. 2
EXAMS COMPARTMENT NO.  1
 IDX        NAME         AQUEOUS MASS   SORBED MASS     PRECIPITATED MASS
   140  CO3              1.109D-03    0.0             0.0
   950  ZN               1.530D-07    0.0             0.0
   732  SO4              3.643D-05    0.0             0.0
   150  CA               3.243D-04    0.0             0.0
   460  MG               8.226D-05    0.0             0.0
   280  FE+2             2.507D-06    0.0             0.0
   600  PB               1.448D-07    0.0             0.0
   540  NI               5.110D-07    0.0             0.0
   231  CU+2             2.277D-06    4.558D-06       5.209E-07
   330  H                1.282D-03    0.0            -1.042E-06
     2  H2O              1.914D-06    0.0             5.209E-07
```

### TABLE 6.17 COMPARISON OF PREDICTED AND OBSERVED COPPER CONCENTRATIONS

| | OBSERVED | | MEXAMS | | |
|---|---|---|---|---|---|
| Station | Dissolved (mg/l) | Total (mg/l)* | Compartment | Dissolved (mg/l) | Total (mg/l)* |
| TM01 | 0. | 0.47 | 1 | 0.15 | 0.47 |
| Wetherells Pond WC | 0. | 0.07 | 3 | 0.15 | 0.44 |
| B | - | 1000.* | 4 | 0.15 | 684.* |
| TM03,TM04 | 0.02 | 0.04 | 5 | 0.11 | 0.34 |
| Falls Pond WC | 0.02 | 0.06 | 7 | 0.088 | 0.27 |
| B | - | 850.* | 8 | 0.088 | 418.* |
| TM06 | 0.02 | 0.02 | 9 | 0.075 | 0.23 |

WC - water column
B - benthos
* Benthic total concentration units are mg/kg

The results show a definite over-prediction of both dissolved and total copper in the water column while the benthic results are slightly low. Since the river flow rates used in this study were higher than average, the likely cause of the discrepancies is either non-representative metal loading rates (i.e., higher than the historical average) or an incorrect model configuration such as not considering all transport processs from the water column to the sediment. It is likely that this system could be calibrated by varying one or more processes so that more metal is present in the sediment (particularly the impoundments), and less in the water column. This would be done by further increasing benthic adsorption relative to the water column and/or increasing the dispersive transfer rates. However, the resulting calibration would be difficult to defend given the uncertainties in hydraulics, metal loading, and observed metal concentrations.

The detailed MINTEQ speciation for the metal of interest (Cu) is shown in Table 6.18 for water column and benthic environments. As expected for a natural system of this type, sorption dominates copper fate, and uncomplexed copper probabaly represents a small fraction of the metal.

The factors which most affect metal fate in Ten Mile River are adsorption and those processes which affect transport within and through the impoundments, including settling of adsorbed metal during high flow. Insufficient knowledge of these factors as well as uncertainty regarding typical flow conditions, impoundment hydraulics, and metal concentrations limited the scope of this study. Based on these conclusions, the following list of recommendations would facilitate a quantitative application:

1) Data collection should be performed during low flow, steady-state conditions, and all data should be collected concurrently whenever possible.

2) Because of their importance, impoundments should be well characterized with regard to hydraulics including dimensions, flows, and estimated sediment trapping efficiencies.

3) Metal concentration data should be accurate to at least 1 ug/l, and routine chemical analyses should include the following: $H^+$, $Na^+$, $K^+$, $Ca^{+2}$, $Mg^{+2}$, $SO_4^{-2}$, $Cl^-$, $PO_4^{-3}$, $NO_3^-$, $NH_4^+$, alkalinity, Eh, and suspended sediment.

TABLE 6.18 TYPICAL SPECIATION OF COPPER IN TEN MILE RIVER

| Species | Water Column % | Benthic % |
|---|---|---|
| $Cu^{+2}$ (aq) | 6 | - |
| Cu-SOH | 67 | 100 |
| $CuCO_3$(aq) | 12 | - |
| $Cu(OH)_2$(aq) | 13 | - |
| $CuHCO_3^+$ (aq) | 2 | - |

4) A thorough equilibrium adsorption analysis should be performed for each metal including precise metal determinations under varying conditions of sediment concentration and total metal to allow application of the Langmuir isotherm adsorption model.

5) Composite sampling of metal discharges should be performed to limit the effect of variable flow and concentration.

6) MEXAMS should be applied in a manner similar to that described here with a refined compartmental configuration and consideration of sediment settling. Calibration of the system could be performed by varying settling rates, water-sediment dispersion, and adsorption coefficients to vary the water column-benthic interaction.

7) Alternately, since this system is extremely complex, requiring major effort in data analysis and reduction to apply MEXAMS, and exhibiting variable loading rates and river flows, one could use a dynamic transport model (including adsorption and sediment transport) to characterize the transport. Subsequent MINTEQ simulations would be performed to obtain more detailed information of metal speciation in selected critical reaches of Ten Mile River, such as near a large point source or in an impoundment.

# SECTION 7

# SEDIMENT SETTLING AND RESUSPENSION IN MEXAMS

Sediment transport is likely to be important in the transport of highly adsorbed and precipitated chemicals in rivers. The significant transport processes include advection and dispersion within the water column, deposition (settling), and scour (resuspension). In many rivers, net deposition over time can lead to effective burial of chemicals within the benthic sediments. EXAMS' steady-state hydraulic simulation does not explicitly consider the processes of sediment settling and resuspension. Currently, river sediment washloads are represented in EXAMS by advective and dispersive sediment transport between water column compartments. Also, bedload transport is represented by flows between benthic compartments which are horizontally adjacent. However, net sedimentation and resulting burial of chemicals must be represented by an artificial 1st-order degradation rate of the chemical in the benthic sediments.

A simple settling/resuspension algorithm has been added to MEXAMS to improve the model's steady-state sediment transport capabilities. This algorithm allows the user to specify steady-state, vertical settling from the water column to benthic compartments and corresponding resuspension. Net deposition of sediment to the benthic compartment is considered; however, net erosion is not permitted. This section documents the incorporation of these new capabilities in MEXAMS including computations added to the code, input, output, and limitations.

## 7.1 OVERVIEW

Settling/resuspension was incorporated in MEXAMS in a manner parallel with existing compartment interconnections (i.e. advective and dispersive transport) in the EXAMS model. A number of rules govern the allowed connections. The required inputs are the source and receiving compartment numbers and parameters characterizing the settling/resuspension flows for each pair. If no pairs are specified, EXAMS does not consider settling. Steady-state sediment mass flow rates are computed as the product of a settling rate (or resuspension rate), a cross sectional area, and the sediment concentration characteristic of the source compartment. Burial from benthic compartments (export from the system) is computed as the net settling into that compartment, i.e. settling minus resuspension. Thus, the sediment mass of the compartment remains constant. Finally, these sediment mass transport rates are included as additional terms in the overall equations for adsorbed chemical transport.

## 7.2 ALLOWED SETTLING INTERCONNECTIONS

A number of rules or restrictions govern the specification of settling interconnections; they are defined below:

1. All compartments must be within the ecosystem; i.e., export may not be explicitly specified. Export from the system is computed as the net settling into a benthic compartment.

2. Connected compartments must be vertically adjacent; i.e., they must have a common interfacial area, and be in the same vertical stack.

3. The pair must be either water-sediment or water-water; sediment-sediment pairs are not permitted.

4. Resuspension may only occur from benthic compartments.

5. Net resuspension from benthic compartments (scour) may not occur.

6. Operationally, the "source" compartment number must be smaller than the "receiving" compartment number; i.e., settling/resuspension is defined as occurring from an upper compartment to a lower compartment.

## 7.3 SETTLING/RESUSPENSION COMPUTATIONS

This section documents the specific computations incorporated into the EXAMS program; all equations and variable names shown below are identical to those in the code. Based on the rules described in Section 7.2, the program determines the valid compartment pairs. For each valid pair, sediment flow due to settling is computed as follows:

$$\mathrm{SETFL}(I,J) = \mathrm{SETLRG}(K) * \mathrm{XSSETG}(K) * \mathrm{SEDCOL}(J) * 1000. \qquad (7.1)$$

where SETFL(I,J) = computed settling flow of sediment from compartment J to compartment I (kg/hr)
SETLRG(K) = settling rate for pair K (m/hr)
XSSETG(K) = cross sectional area for pair K
SEDCOL(J) = sediment mass per volume of water in compartment J (kg/l)
1000. = units conversion factor

Next, resuspension flow is computed for this compartment pair as shown below. Note that the porosity of the benthic compartment has been accounted for by the inclusion of WATVOL/VOLG in the equation.

$$\mathrm{SETFL}(J,I) = \mathrm{RSUSPG}(K)*\mathrm{XSSETG}(K)*\mathrm{SEDCOL}(I)*\mathrm{WATVOL}(I)/(\mathrm{VOLG}(I)*8.76\mathrm{E}6)) \qquad (7.2)$$

where SETFL(J,I) = computed resuspension flow of sediment from compartment J to compartment I (kg/hr)
RSUSPG(K) = resuspension rate for pair K (mm/yr)
XSSETG(K) = cross sectional area for pair K (m2)
SEDCOL(I) = sediment mass per volume of water in compartment I (kg/l)
WATVOL(I) = volume of water in compartment I (l)
VOLG(I) = volume of compartment I (m3)
8.76E6 = units conversion factor

The net settling into a benthic compartment of a water-sediment pair is assumed by the program to represent a net export of sediment (burial) from the ecosystem. This export is computed as follows:

$$\mathrm{SETOUL}(I) = \mathrm{SETFL}(I,J) - \mathrm{SETFL}(J,I) \qquad (7.3)$$

where SETOUL(I) = the mass of sediment lost from the ecosystem due to settling into compartment I (kg/hr)

The above quantity is checked to ensure that net burial rather than scour is occurring.

Finally, settling/resuspension flows are included in the evaluation of 1st-order toxicant loss rates by adding the sediment flows computed above to the appropriate equations.

These equations, with the new terms included are:

```
EXPOKL(J) = WATOUL(J)*ALPHA(17,J)+SEDOUL(J)*              (7.4)
    (ALPHA(16,J)+ALPHA(18,J))/SEDCOL(J)+WATOUL(J)*
    ALPHA(19,J)*PLRAG(J) + SETOUL(J)*ALPHA(18,J)/SEDCOL(J)

INTOUL = INTOUL+WATFL(I,J)*ALPHA(17,J)+SEDFL(I,J)*        (7.5)
    (ALPHA(16,J)+ALPHA(18,J))/SEDCOL(J)+WATFL(I,J)*
    ALPHA(19,J)*PLRAG(J) + SETFL(I,J)*ALPHA(18,J)/SEDCOL(J)

INTINL(I,J) = WATFL(J,I)*ALPHA(17,I)+SEDFL(J,I)*          (7.6)
    (ALPHA(16,I)+ALPHA(18,I))/SEDCOL(I)+WATFL(J,I)*
    ALPHA(19,I)*PLRAG(I) + SETFL(J,I)*ALPHA(18,I)/SEDCOL(I)
```

where EXPOKL(J) = loss rate for compartment J due to export from the compartment out of the ecosystem (1/hr)

INTOUL = the rate representing intercompartment flow of chemical out of a compartment (1/hr)

INTINL(I,J)= the rate representing intercompartment flow of chemical into a compartment (1/hr)

ALPHA(18,J)= the fraction of chemical adsorbed to sediment in compartment J

## 7.4 INPUT AND OUTPUT

Input data required to include these settling flows in MEXAMS are the following:

NSPEC3 - number of settling/resuspension pairs

JSETLG(NSPEC3) - source compartment number for each pair

ISETLG(NSPEC3) - receiving compartment number for each pair

SETLRG(NSPEC3) - sediment settling rate for each pair (m/hr)

RSUSPG(NSPEC3) - sediment resuspension rate for each pair; not required for water-water pairs (mm/yr)

XSSETG(NSPEC3) - cross sectional area for settling/resuspension for each pair (m2)

These parameters are added to the end of the EXAMS input, and their input formats are identical to those for specifying advective and turbulent interconnections. Table 7.1 is an example of settling/resuspension input. This example specifies settling/resuspension between all water column and benthic compartment pairs of an eight-compartment ecosystem. The variable names and line formats are shown at the right.

TABLE 7.1 SEDIMENT SETTLING AND RESUSPENSION INPUT

```
    4                                                NSPEC3   (I5)
    1    3    5    7                                 JSETLG   (20I5)
    2    4    6    8                                 ISETLG   (20I5)
     2.450     3.500     3.100     2.500             SETLRG   (8F10.0)
       1.5       1.5       1.5       1.5             RSUSPG   (8F10.0)
    2.5E+4    4.0E+4    1.9E+3    5.5E+4             XSSETG   (8F10.0)
```

The settling interconnections and input parameter values are printed in Table 8.5 of the EXAMS output. The format is identical to Table 8 (Turbulent interconnections). The increased 'Sediment Flows' for compartments affected by settling are shown in Table 9 of the EXAMS output. The sediment 'Residence Times' (Table 9) will also be modified.

# SECTION 8

# RECOMMENDATIONS

## 8.1 ENHANCEMENTS

As recommended in the MEXAMS user's manual, available thermodynamic data for antimony, berylium, chromium, mercury, selenium, and thallium should be incorporated into the MINTEQ data base. This would complete the data base for all of the priority pollutant metals, and would greatly expand the applicability of MEXAMS.

The ability of the model to simulate the effect of organic complexation is a particular limitation. This effect varies from one surface water to another and needs to be examined in more detail. For example, using the model and varying the concentration of EDTA in the MINTEQ files, the effect on adsorption in compartment one for copper, zinc and lead could be described (Figure 8.1).

Further research into incorporating kinetic factors into models of this type would help overcome problems related to assuming equilibrium with respect to precipitation/dissolution, redox, and adsorption phenomenon. Including kinetics would expand model applications to non-steady-state systems such as systems with dynamic storm loading, shock loading and other transient loading. Obviously, a more complicated transport model to describe sediment transport and highly variable flows and water quality conditions would expand the usefulness of the model.

Another area of improvement to the model concerns the persistence calculation. The program was designed to calculate how long it would take to purify (very low concentration) the ecosystem of organic contamination. For metals there is a particular baseline concentration due to background sources, and it would be useful to calculate the time required to achieve this certain concentration. This concentration could also correspond to a toxic level for a certain aquatic specie, or a desired concentration level, as required by some regulatory agency. Flexibility could be

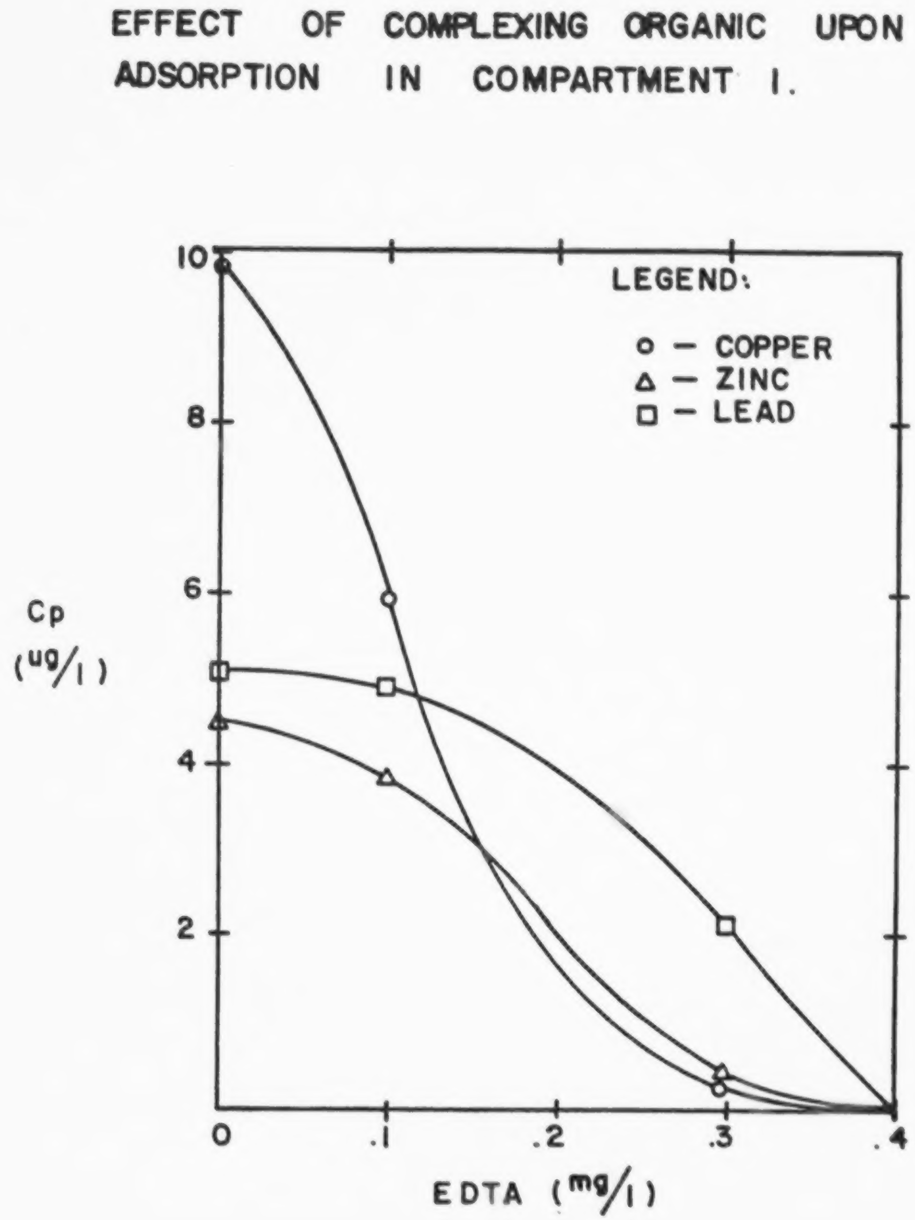


Figure 8.1 The effect of a complexing organic upon adsorption of copper in compartment 1.

maintained by including an input parameter in the MISP input file. This parameter would correspond to the final concentration desired by the programmer (i.e., the concentration due to upstream loadings). To simulate anticipated concentrations within the water column prior to pollutant loadings, the point source chemical loads were removed and the model was utilized to obtain concentrations due to upstream loadings only. A comparison of the model results is presented in Figure 8.2.

## 8.2 DOCUMENTATION

As described in Section 2, the MEXAMS documentation package consists of three volumes which separately document MINTEQ, EXAMS, and the complete MEXAMS program (including MISP). Application of MEXAMS necessitates reference to various sections of all three volumes. Our recommendations for the MEXAMS documentation are 1) the reorganization of the "Guidelines for Use" section of the MEXAMS user's manual to facilitate MINTEQ input development, 2) incorporation of case study tests and enhancements contained in this document, and 3) elimination of the computer system-specific (i.e. PDP-11/70) guidelines where appropriate.

The documentation which describes MISP/MINTEQ input preparation and parameter development should be reorganized and expanded. First, information from several sections of the documentation should be combined in this section. Currently, it is necessary to consult several sections in the documentation to locate the information required to develop input for simulating adsorption as well as other MINTEQ options. The reorganized section (Section 6 of the MEXAMS user's manual) would be partly created by combining the descriptive information on MISP and MINTEQ input, which is currently presented in that section, with the "Description of the MINTEQ Input File" in Appendix C. Additional guidance on MINTEQ input from the MINTEQ user's manual and this document would also be included.

Second, the modified input description section should be organized by subjects and parameters. Use of descriptive headings to delineate input sections and parameters is recommended rather than focussing on the series of questions which MISP presents to the user. While reference to the specific question numbers could be included where appropriate, descriptive headings would make it easier to locate information related to a particular subject or parameter. Model users who don't have access to the interactive capabilities of MISP would find this modified section especially useful.

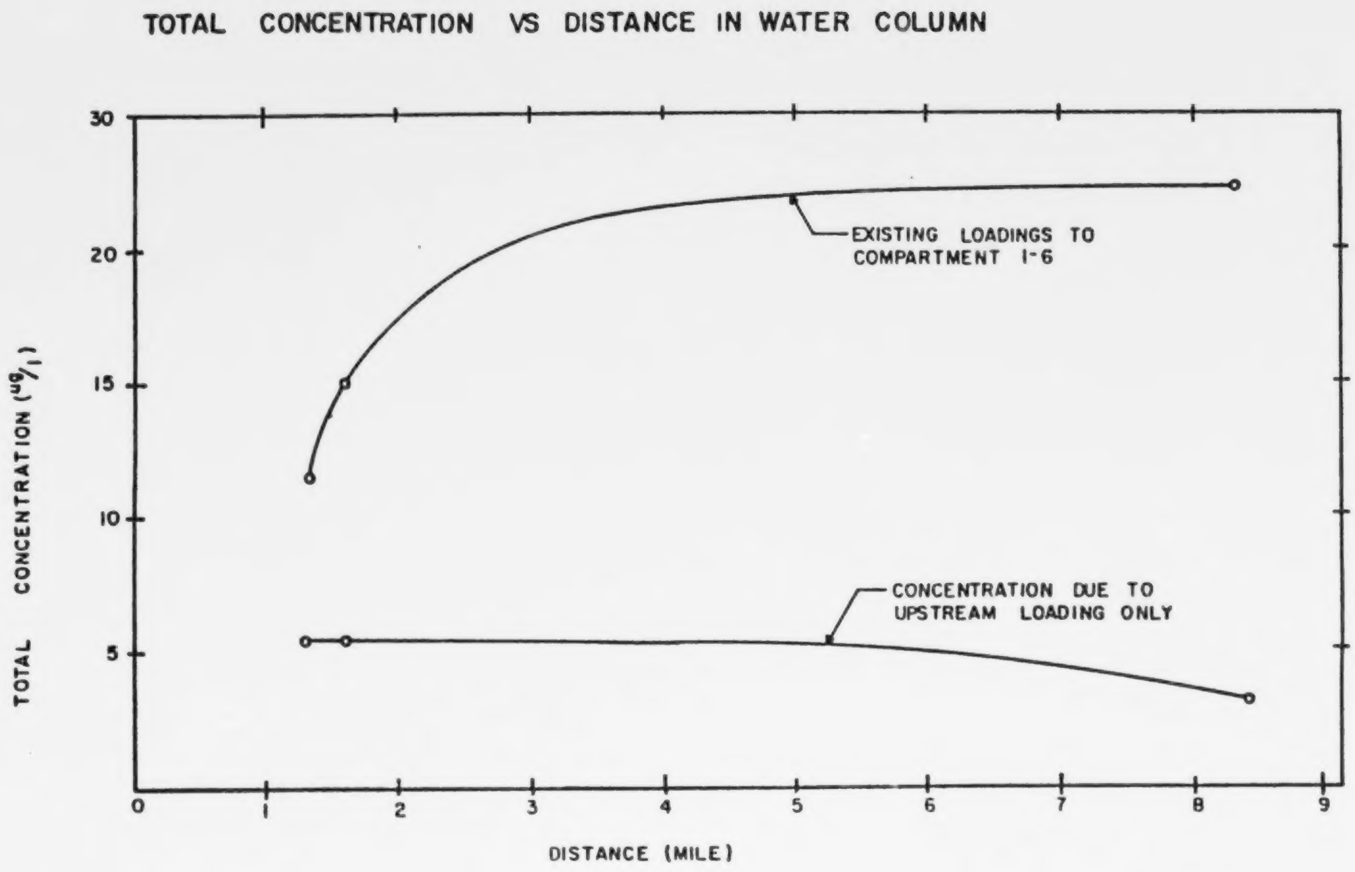


Figure 8.2 Total metal concentration in water column compartments under hypothetical natural loading.

One or more of the case studies described in this document should be incorporated into the MEXAMS user's manual. This would provide users with invaluable guidance on input parameter development and general input preparation. Also, recent enhancements and modifications such as sediment settling/resuspension should be documented, since they are not included in the EXAMS User's Guide.

Currently, the MEXAMS documentation is oriented toward using the model on a DEC PDP-11/70 computer system. Potential users will have access to other computers such as IBM, Prime, HP, etc. Recent developmental work on MEXAMS such as the case study tests and sediment settling modifications was performed on an IBM version of the program. Also, further development on the PDP-11/70 version is unlikely due to size limitations of this system. More appropriate documentation would be general, non-computer-system-specific, and would include any system-specific limitations, differences and operational instructions in appendices.

## 8.3 CODE INTEGRATION

The PDP-11/70 version of MEXAMS consists of three separate programs which schedule each other in various sequence depending on user options. Input controlling the overall model operation such as metal specification and MINTEQ/EXAMS sequencing is obtained during a preliminary interactive session. The IBM version of MEXAMS currently being used by EPA was adapted from the PDP-11/70 version by integrating these programs into one large program, replacing the scheduling sequence with appropriate subroutine CALLs and requiring the interactive responses to be read from a file. This integration resulted in some errors and inefficiencies in MEXAMS operation. For example, the PDP-11/70 version of MINTEQ, which was adapted for IBM, uses a direct access file to store a large matrix. The extensive I/O to this file resulted in inefficient and expensive model execution. Consequently, the program was modified by placing the matrix in memory. However, a more efficient version of MINTEQ, which already stored this matrix in memory, is available. A second problem with the integrated version is that some sequencing errors occur when using the persistence computations in EXAMS. While the cause and extent of these errors are unknown, the persistence calculations are currently not operating correctly in the IBM version.

It is recommended that the MISP, EXAMS, and MINTEQ programs be re-integrated to correct these problems and add additional enhancements. The following are specific recommendations with regard to this re-integration:

1) Correct the sequencing errors which presently occur when executing the EXAMS persistence routines.

2) Use the original version of MINTEQ which maintains its primary solution matrix in memory rather than a file.

3) Use a 100-compartment version of EXAMS; the current MEXAMS contains a 10-compartment EXAMS which is limiting for some applications.

4) Replace the MISP "interactive" input format with a standard format. This input directs the overall model operation such as MINTEQ/EXAMS sequencing, metal identification, and persistence computations.

## 8.4 MODEL USAGE

An important recommendation with respect to initial model use is the development of a representative data base which characterizes physical, chemical and biological attributes of the environment. This includes instantaneous measures for major water quality constituents; major ions (Ca, Mg, Na, K, Cl, SO4, HCO3), minor ions (Mn, Fe, Si, B, N, P, F) and important trace metals (Zn, Cu, Cr, Cd, Pb, etc.). An estimate of organic complexing capacity of the system for particular priority pollutant metals would be useful for sediment characteristics and metal details (concentrations, partition coefficients, adsorption behavior, etc.) are essential along with an understanding of the hydrologic characteristics, sediment transport and pollutant loadings from various sources.

# REFERENCES

Balistrieri, L.S. and J.W. Murray. 1981. "The Surface Chemistry of Goethite in Major Ion Seawater," Amer. J. Sci., Vol. 281, pp. 788-806.

Balistrieri, L.S. and J.W. Murray. 1982. "The Adsorption of Cu, Pb, Zn, and Cd on Goethite from Major Ion Seawater," Geochim. Cosmechim. Acta, Vol. 46, pp. 1253-1265.

Beck, M.B. 1983. "A Procedure for Modeling," *Mathematical Modeling of Water Quality*, G.T. Orlob (Ed.) International Institute for Applied System Analysis Series, John Wiley and Sons, New York, N.Y. pp. 11-41.

Benjamin, M.M. and J.O. Leckie. 1981. "Conceptual Model for Metal - Ligand - Surface Interactions During Adsorption." J. Environ. Sci. Technol. 15, 1050.

Benjamin, M.M. and J.O. Leckie. 1982. "Effects of Complexation by Cl, SO4, and S2O3 on Adsorption Behavior of Cd on Oxide Surfaces." Environ. Sci. Technol., Vol. 16, p162-170

Bryson, R.A. and F.K. Hare. 1974. *Climates of North America*, Elsevier Scientific, New York, NY, p. 213.

Burns, L.A., D.M. Cline and R.R. Lassiter. 1982. *Exposure Analysis Modeling System (EXAMS): User Manual and System Documentation*, U.S. Environmental Protection Agency, Environmental Research Laboratory, Athens, GA.

Chappell, W.R. 1984. "Summary of Health and Environmental Research: Oil Shale," *Synthetic Fossil Fuel Technologies*, Butterworth Publishers, MA. pp. 55-109.

Chapra, S.C. and K.H. Reckhow. 1983. *Engineering Approaches for Lake Management Vol I*, Butterworth Publishers, MA. pp. 29-42, 250-299.

Chapra, S.C. and K.H. Reckhow. 1983. *Engineering Approaches for Lake Management Vol II*, Butterworth Publishers, MA. pp. 65-66, 312-330, 435-455.

Curtis (1982) Personal Communication.

Curtis, M.D. and L.E. Dunbar. 1984. Total Maximum Daily Load Development Using an Integrated Allocation Approach, Proceedings of ASCE Environmental Division National Conference held in Los Angeles, CA.

Davis, J.A. and J.O. Leckie. 1978. "Effect of Adsorbed Complexing Ligands on Trace Metal Uptake by Hydrous Oxides." Environ. Sci. Technol, 12, 1309.

Davis, J.A., R.O. James and J.O. Leckie. 1978. "Surface Ionization and Complexation at the Oxide/Water Interface. 1. Computation of Electrical Double Layer Properties in Simple Electrolytes," J. Coll. Inter. Sci. Vol. 63(3), pp. 480-499.

Davis, J.A. and J.O. Leckie. 1978. "Surface Ionization and Complexation at the Oxide/Water Interface. 2. Surface Properties of Amorphous Iron Oxy Hydroxide and Adsorption of Metal Ions," J. Coll. Inter. Sci. Vol. 67(1), pp. 90-107.

Davis, J.A. and J.O. Leckie. 1980. "Surface Ionization and Complexation at the Oxide/Water Interface. 3. Adsorption of Anions," J. Coll. Inter. Sci. Vol. 74(1), pp. 32-43.

Donigian, A.S. 1982. "Field Validation and Error Analysis of Chemical Fate Models," Modeling the Fate of Chemicals in the Aquatic Environment, K.L. Dickson, A.W. Maki and J. Cairns, Jr. (Eds.) Ann Arbor, MI. pp. 303-324.

EPRI. 1984. "Chemical Attenuation Rates, Coefficients, and Constants in Leachate Migration, Volume 1: A Critical Review," Electric Power Research Institute, Palo Alto, CA.

Felmy, A.R., D.C. Girvin and E.A. Jenne. 1984a. MINTEQ--A Computer Program for Calculating Aqueous Geochemical Equilibria, U.S. Environmental Protection Agency, Environmental Research Laboratory, Athens, GA.

Felmy, A.R., S.M. Brown, Y. Onishi, S.B. Yabusaki and R.S. Argo. 1984b. MEXAMS--The Metals Exposure Analysis Modeling System, U.S. Environmental Protection Agency, Environmental Research Laboratory, Athens, GA.

Forstner, U. and G.T.W. Wittman. 1981. Metal Pollution in the Aquatic Environment, Springer-Verlag, New York, N.Y.

Grant, C.V. 1983. "Energy Development and Riparian Management in a Cold Desert Ecosystem," *Aquatic Resources Management of the Colorado River Ecosystem*, V. Dean Adams and V.A. Lamarra (Eds.), Ann Arbor Science Publishers, Inc., Ann Arbor, MI. pp. 289-301.

Huang, C.P., H.A. Elliott and R.M. Ashmead. 1977. "Interfacial Reactions and the Fate of Heavy Metals in Soil-Water Systems." J. Water Pollut. Control Fed. 49, 745.

LaPoint, T.W., S.M. Melancon and M.K. Morris. 1984. "Relationships Among Observed Metal Concentrations, Criteria, and Benthic Community Structural Responses in 15 Streams," J.W.P.C.F., Vol. 56(a), pp. 1030-1038.

Mass. D.W.P.C. 1973. *Ten Mile River 1973 Water Quality Survey Data, Part A*, Massachusetts Water Resources Commission, Division of Water Pollution Control, Westborough, MA.

Mass. D.W.P.C. 1975. *Ten Mile River 1973 Water Quality Survey Data, Part D*, Massachusetts Water Resources Commission, Division of Water Polution Control, Westborough, MA.

Mass. D.W.P.C. 1982. *Ten Mile River Basin 1981 Water Quality Survey Data*, Massachusetts Department of Environmental Quality Engineering, Division of Water Pollution Control, Westborough, MA.

Medine, A.J. 1983. "Potential Impacts of Energy Development Upon Water Quality of Lake Powell and the Upper Colorado River," *Aquatic Resources Management of the Colorado River Ecosystem*, V. Dean Adams and V.A. Lamarra (Eds.) Ann Arbor Science Publishers, Inc., Ann Arbor, MI. pp. 399-424.

Medine, A.J. and M.F. Conway. 1982. *Heavy Metal Interactions and Dynamics in Simulated Naugatuck River Microcosms*, Institute of Water Resources, University of Connecticut.

Medine, A.J. and D.B. Porcella. 1980. "Heavy Metal Effects on Photosynthesis/Respiration of Microecosystems Simulating Lake Powell, Utah/Arizona," *Contaminants and Sediments, Vol. II*, Robert A. Baker (Ed.), Ann Arbor Science Publishers, Inc., Ann Arbor, MI. pp. 355-390.

Morel, F.M.M. 1983. *Principles of Aquatic Chemistry*,John Wiley and Sons, New York, NY.

Orlob, G.T. 1983. *Mathematical Modeling of Water Quality*, John Wiley and Sons, New York, NY. pp. 425-460.

Schindler, P.W., B. Furst, R. Dick, and P.U. Wolf. 1976. "Ligand Properties of Surface Silanol Groups: I. Surface Complex Formation with Fe+2, Cu+2, Cd+2 and Pb+2 " J. Colloid Interface Sci. 55(2)469.

Snoeyink, V.L. and D. Jenkins. 1980. *Water Chemistry*. John Wiley and Sons, New York, NY.

St. John, J.P. and D.M. DiToro. 1981. "Analysis of Fate of Chemicals in Receiving Waters - Phase I." Prepared for CMA by HydroQual, Inc., Mahwah, New Jersey.

Stollenwork, K.G. and D.D. Runnells. 1981. "Composition of Leachate from Surface-Retorted and Unretorted Colorado Oil Shale," Environ. Sci. Technol., 14,11.

U.S. Environmental Protection Agency. 1980. *Ambient Water Quality Criteria for Copper*, EPA 400/5-80-036.

U.S. Geological Survey. 1983. "Water Resources Data - Connecticut."

VTN Colorado, Inc. 1977. "Final Environmental Baseline Report," White River Shale Project, October.

Zanella, E.F. 1982. "Shifts in Caddisfly Species Composition in Sacramento River Invertebrate Communities in the Presence of Heavy Metal Contamination," Bull. Environ. Contam. Toxicol., 29:306-312.